THE KINETIC CHARACTERIZATION OF THE POLYMERIZATION OF ISOPRENE IN BENZENE INITIATED BY BUTYL LITHIUM AS A FIRST STEP IN THE SYNTHESIS OF BLOCK COPOLYMERS

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Abstract—The kinetics of the initiation and propagation steps in the polymerization of isoprene in benzene, initiated by butyl lithium as a first step in the synthesis of block copolymers has been examined. The rate of initiation is first order with respect to butyl lithium. A slow initial reaction is followed by an acceleration of the rate as polymer is generated. The sigmoidal rate curve appears to be characteristic of the initiation step and not due to termination products. The rate of propagation is shown to be a half order with respect to the concentration of growing chains, indicating a dimeric association of the polymer.

INTRODUCTION

Studies on the solution properties of block copolymers have demonstrated the desirability of developing better synthetic methods if these investigations are to be worthwhile.[1] The strict tolerances imposed on homogeneity of the product, in molecular weight, composition, absence of extraneous homopolymer, and possibly even micro structure, place very high demands on skill and technical ingenuity.

Certain essential conditions must be observed in the two stages of the preparation. Firstly, all of the monomer in the first stage must have been consumed before the second monomer can be added. Secondly, the initiation step must be fast compared with the propagation step if the molecular weight distribution is not to be broad. Alternatively, a polymer seed of low molecular weight may be prepared and then added to the bulk of the monomer for the propagation step. This method still requires a fast initiation in order that all of the initiator be consumed. It may be possible to add small amounts of polar substances such as tetrahydrofuran since Worsfold and Bywater[2] have found that these substances cause a large increase in initiation with little increase in propagation. The third condition is that impurities which will cause initiator destruction or the destruction of growing chains must be reduced to negligible proportions. The problem reaches significant proportions when high molecular weight products are desired since the initiator concentrations employed are of the order of 10^{-4} molar and spurious termination must be at least two orders smaller than this. Finally, in the second stage of the polymerization the second monomer must be added without the addition of terminating material to avoid contamination of the product with homopolymer from the first step.

In this study the solvent benzene was chosen because of the stereospecificity of the polymer formed when isoprene is polymerized by lithium alkyls in benzene.[3, 4] The configuration of the polymer product is mainly *cis* 1,4 although the exact proportion of the micro-structure so far reported appears to be in poor agreement. This is probably due, in part, to the different methods of analysis employed.[4] The lack of published data in this solvent led us to examine both the initiation and progapation steps. The concentration of polyisoprenyl lithium was determined spectrophotometrically in the visible range and was based on determinations of "living ends" using the Volhard
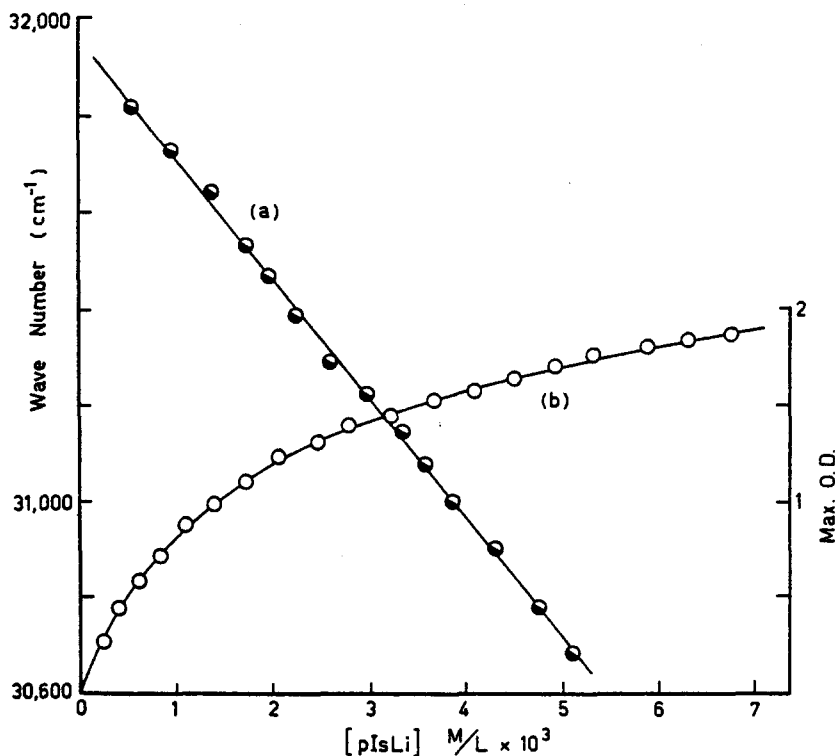

Fig. 1.(a). Frequency of the absorption maximum vs. the concentration of polyisoprenyl lithium.
(b). The optical density of the absorption maximum vs. the concentration of polyisoprenyl lithium.

methyl iodide analysis. End points were detected both colorimetrically and by the more direct electrometric method. Consumption of monomer was followed by dilatometry.

Spectrophotometric studies of the coloured polyisoprenyl lithium showed a hypsochromic shift of the maximum absorption on dilution. Within the range of concentrations measured (5×10^{-4} M–5×10^{-3} M) the drift was linear [Fig. 1.(a)]. This concentration dependence rather suggests that a whole spectrum of polymerization intermediates, complexed with the solvent, is involved. The extinction coefficients ranged from $\epsilon = 500$ at low concentrations (up to $2 \cdot 5 \times 10^{-3}$ M) to $\epsilon = 280$ at the highest concentration $1 \cdot 0 \times 10^{-2}$ M. Comparing these data with the kinetic results, the average association

number for the growing chain appears to change from the dimeric form in dilute solution to trimer or tetramer in more concentrated solution. Sinn has reported the existence of the monomer form at very low concentrations and an even higher association number in concentrated solutions of n-heptane. Conductivity studies in these solutions indicate the virtual absence of free ions.[5] A calibration curve [Fig. (1b)] was constructed from the observed O.D. at the maximum at various concentrations and the concentrations of polyisoprenyl lithium were computed from the maxima observed at each stage of the polymerization.

EXPERIMENTAL

Benzene (Univar A.R. grade) was dried over sodium wire, refluxed over calcium hydride and fractionally distilled. After degassing on the vacuum line a quantity of butyl lithium was added and styrene distilled into the vessel. The characteristic red colour developed after termination of adventitious material. Benzene for use as solvent was flash distilled from this reservoir.

LEGEND

R   Reaction vessel
P   Purging solution
In   Initiator solution
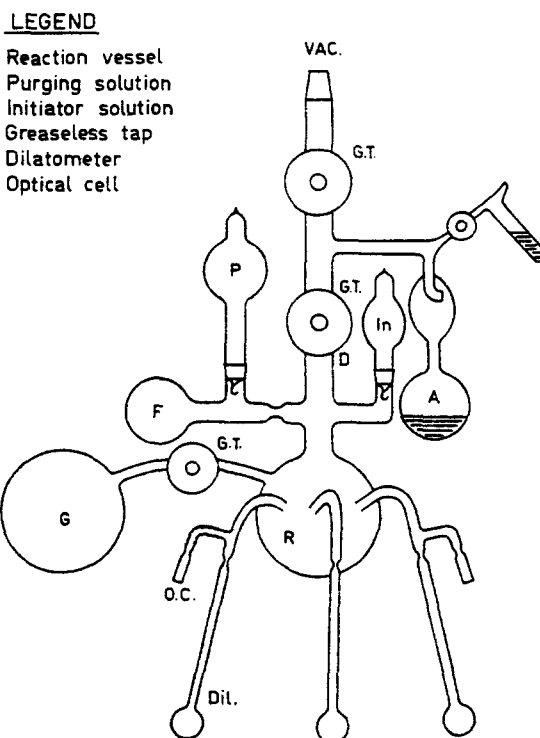G.T.   Greaseless tap
Dil.   Dilatometer
O.C.   Optical cell

FIG. 2. The reaction vessel.

Monomers were dried over calcium hydride, degassed and distilled. The middle fraction was distilled on to fresh calcium hydride and allowed to stand for 24 hr. The process was repeated three times and finally stored at $-10°$ in the dark. Methyl iodide was subjected to the same procedure before use.

Purging solutions were prepared from styrene and butyl lithium in benzene and stored in 50-ml ampoules with twist break seals ready for use. Butyl lithium was prepared by slow addition of a solution of butyl chloride in benzene to lithium shavings in benzene in an atmosphere of oxygen free nitrogen. After 12 hr the concentrated butyl lithium solution was decanted into a retort fitted with a greaseless tap. Ampoules of butyl lithium were sealed off at this stage for use in determining the initiation rate. Polyisoprenyl lithium "seed" was prepared using this butyl lithium. After degassing, a calculated

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quantity of isoprene was added and the formation of isoprenyl lithium followed spectrophotometrically in sealed optical cells. Having determined the concentration of the initiator "seed", predetermined volumes were sealed off in ampoules. The initiator seed prepared had an average molecular weight of about 3000 when all butyl lithium had been consumed. Analysis of the concentration of "seed" was effected by adding methyl iodide and determining the concentration of lithium iodide resulting. The solutions were titrated with excess silver nitrate and back titration with ammonium thiocyanate or more commonly a potentiometric titration was employed by titrating the silver nitrate against the lithium iodide directly. This method proved to have the greater accuracy.

Propagation was followed by dilatometry. The solutions were prepared in the vessel shown in Fig. 2 which allowed the purging of the apparatus including dilatometers and spectrophotometer cells. The partially spent purging solution was tipped into bulb F and the vessel removed from the apparatus. Monomer and solvent were flash distilled into A and purging solution added through a greaseless tap until a permanent colour persisted. The solution was washed around the upper part of the vessel and then tipped back into A. Monomer and solvent were then distilled into the reaction flask, the large greaseless tap at D closed and initiator seed added. Samples for dilatometry and spectrophotometry were then sealed off. The reaction mixture was isolated in bulb G for the second stage of the preparation.

RESULTS

A preliminary examination of this system indicated that initiation was complete when an average of 40 monomer units had been consumed for each molecule of butyl lithium, a value which is much smaller than the several hundred units found in cyclohexane by
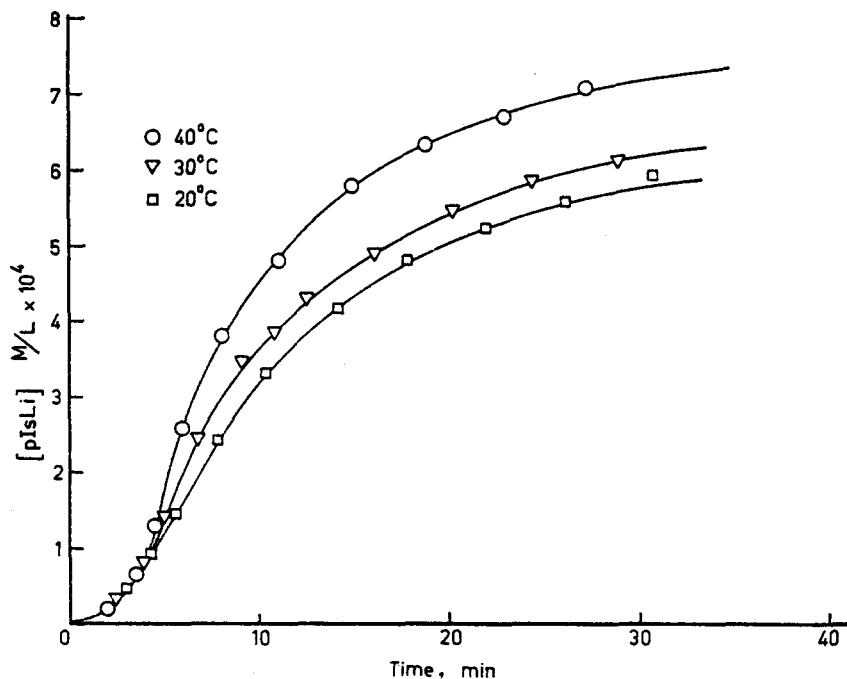

FIG. 3. Initiator conversion-time curves for the formation of polyisoprenyl lithium at several temperatures.

Worsfold and Bywater.[2] This value is simply the ratio of the total monomer consumed at complete initiation to the total initiator generated. The polymerization was followed spectrophotometrically and by dilatometry simultaneously. These values lead to a considerable improvement in homogeneity over the reaction in cyclohexane, nevertheless a reduction in monomer consumed during initiation is desirable.

The initiator time–conversion curves (Fig. 3) are sigmoidal due to an initial induction period which is followed by an acceleration of the rate. The butyl lithium initially added to the system was found to correspond with the final concentration of polyisoprenyl lithium and therefore it must be concluded that the induction period is characteristic of the initiation step.
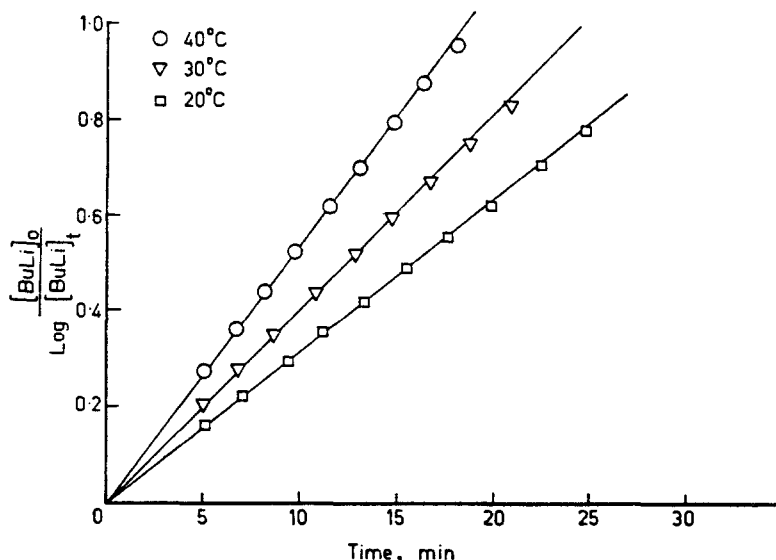

FIG. 4. First-order plots of the conversion of butyl lithium to polyisoprenyl lithium at several temperatures.

Excellent first–order plots of the initiation rate after the induction period were obtained (Fig. 4). The energy of activation and pre-exponential factor were obtained from the temperature dependence of the rate of initiation and the apparent rate constant for initiation is then

$$k_1 = 10^{2 \cdot 0} \exp -\frac{4 \cdot 300}{RT}$$

and at 30° is $8 \cdot 04 \times 10^{-2}$ litre mole^{-1} min^{-1}. Worsfold and Bywater[2] have proposed that a complex of the polyisoprenyl lithium and butyl lithium is an active polymerization agent. The low pre-exponential factor observed here is consistent with the large negative entropy to be associated with formation of such a complex. It seems plausible that the ion pairs Bu$^-$Li$^+$ may begin the initial slow reaction which is rapidly catalyzed by the complex being formed.

The rate of propagation was followed by dilatometry after all of the butyl lithium was consumed and the optical density of the solution remained constant. Good first-order plots were obtained for the consumption of monomer over at least four half-life times (Fig. 5). The rate of propagation is therefore

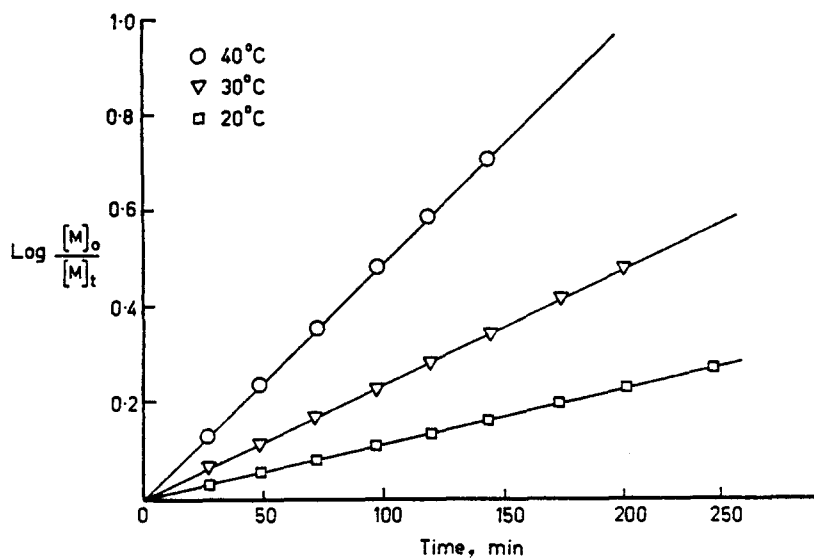$$-\frac{d[M]}{dt} = k_2 \text{ [polyisoprenyl lithium]}^n \text{[isoprene]}^{1 \cdot 0}$$

FIG. 5. First-order plots of the consumption of monomer in the propagation reaction at several temperatures.
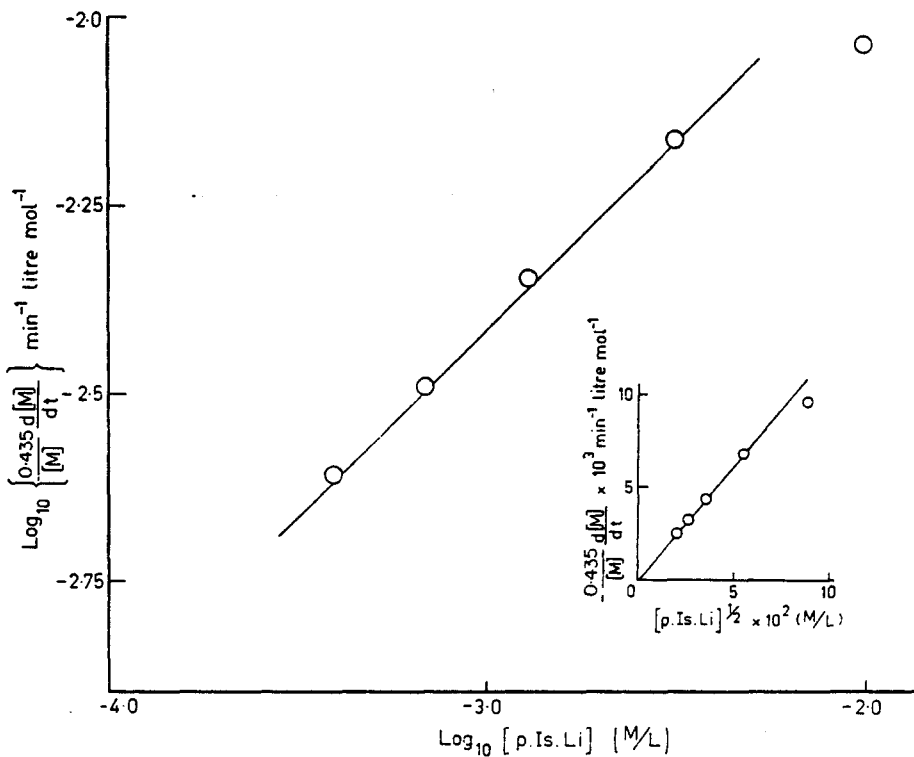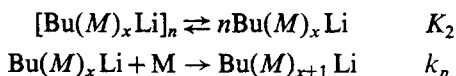

FIG. 6. $\log_{10}\left[-\dfrac{0\cdot435}{[M]}\dfrac{d[M]}{dt}\right]$ vs. $\log_{10}$ [polyisoprenyl lithium].

Inset: $-\dfrac{0\cdot435}{[M]}\dfrac{d[M]}{dt}$ vs. [polyisoprenyl lithium]$^{\frac{1}{2}}$.

in accordance with the mechanism

$$[\mathrm{Bu}(M)_x\mathrm{Li}]_n \rightleftharpoons n\mathrm{Bu}(M)_x\mathrm{Li} \qquad K_2$$

$$\mathrm{Bu}(M)_x\mathrm{Li} + M \rightarrow \mathrm{Bu}(M)_{x+1}\mathrm{Li} \qquad k_p$$

in which the growing chain is assumed to be strongly associated. The apparent rate constant is therefore a function of the equilibrium constant. In Fig. 6 a plot of $\log_{10} - (1/[M])/(\mathrm{d}[M]/\mathrm{d}t)$ vs. $\log_{10}[\mathrm{p\cdot Is\cdot Li}]$ has been constructed. The slope of the line drawn through the experimental points is $0\cdot5$ corresponding to a half order with respect to polyisoprenyl lithium. The points suggest that a change in slope at higher concentrations might be expected but the data are inconclusive and further study is under way to examine the kinetics in this system.

The Arrhenius constants have been determined from the temperature dependence of the rates and the apparent rate constant for propagation is:

$$k_2 = 10^{9\cdot0}\exp-\frac{13,300}{RT}$$

and at 30° the experimental value is $7\cdot7 \times 10^{-2}$ litre mole^{-1} min^{-1}.

Inset is the plot of $-(1/[M])/(\mathrm{d}[M]/\mathrm{d}t)$ vs. [polyisoprenyl lithium]$^{\frac{1}{2}}$ which demonstrates the absence of adventitious termination.

DISCUSSION

Efforts to determine the absolute rate constants in anionic polymerization have been aggravated by the existence of complex association equilibria, and work done on this problem has been reviewed recently by Bywater.[4] Whilst little data have been published on initiation, several attempts have been made to evaluate k_p. Two lines of approach have been used. Sinn[7, 8] has worked at low concentration and assumed that only the unassociated form of the growing chain exists. Morton[9,19] has attempted to determine the equilibrium constant K_2 by an independent method. Bywater concludes that, despite the ingenuity shown by these workers, no accurate value for k_p has yet been obtained. Despite this handicap, it is instructive to determine the apparent rate constants in a given system in order that k_1 and k_2 may be compared.

It is seen from the measured rate constants at 30° that the rates of initiation and propagation are approximately equal and the Arrhenius factors show that polymerization at lower temperatures improves the ratio in favour of initiation. The addition of small amounts of polar substances such as T.H.F. has been shown to increase initiation with little change in propagation. This might be used to advantage in providing a narrower molecular weight distribution, however the resulting change in microstructure may be a disadvantage when examining solution properties.

It can be concluded from this study that the system investigated will provide a satisfactory first stage for the synthesis of homogeneous block copolymers of predictable molecular weight, composition and purity. The second stage is now being investigated.

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Résumé—La cinétique des mesures d'initiation et de propagation dans la polymérisation de l'isoprène en benzène, a débuté par le butyllithium comme première mesure dans la synthèse de blocs de copolymères, et a été examinée. Le taux d'initiation est de premier ordre en ce qui concerne le butyllithium. Une réaction initiale lente est suivie par une acceleration du taux à mesure que le polymère est généré. Le taux de courbe sigmoidale semble être caractéristique des mesure d'initiation, et non pas dû à des produits de terminaison. Le taux de propagation est démontré comme étant d'un ordre moyen par rapport à la concentration de chaînes en croissance, indiquant une association dimérique du polymère.

Sommario—La cinetica del progresso dell'iniziazione e propagazione nella polimerizzazione di isoprino nella benzina, iniziata da bitillutio come primo passo nella sintesi di copolimeri in blocco, è stata-esaminata. La quantità di iniziazione è di primo ordine rispetto al bitillutio. Una leggera iniziale reazione è seguita da una accelerazione della quantità quando il polimero è generato. La curva della quantità sigmoidale appare caratteristica del passo di iniziazione e non dovuta a prodotti di terminazione. La quantità di propagazione dimostra di essere di ordine dimezzato rispetto alla concentrazione di catene crescenti, indicando un'associazione dimerica del polimero.

Zusammenfassung—Die kinetische Theorie der Einleitungs und Ausbreitungsstufen der Polymerisation von Isopren in Benzol, welche von Butyllithium als eine erste Stufe in der Synthese von Block-Mischpolymerisation eingeleitet ist, wurde untersucht. Die Einleitungsgeschwindigkeit ist mit Hinsicht zu Butyllithium, von der ersten Ordnung. Eine langsame Anfangsreaktion wird als Polymer erzeugt, gefolgt bei einer Beschleunigung der Geschwindigkeit. Die sigmaförmige Geschwindigkeitskurve scheint eine Charakteristik der Einleitungsstufe zu sein und wird nicht von Endprodukten veranlasst. Es wird gezeigt, das die Ausbreitungsgeschwindigkeit von halber Ordnung, in Hinsicht zu der Konzentration von wachsenden Ketten, ist, welche eine dimerische Zuordnung des Polymers anzeigt.