of the merits and flaws of the models, as well as their more rigorous application to hetero-disperse systems, will be reported in the subsequent publication.

In conclusion it may be stated that the dilatometric method of measuring the ratio k_t/k_p has been found effective over a viscosity range from 0.4 to 200 cp., and values of the termination and propagation rate constants have been calculated from this ratio over the range. Whereas the propagation (and also the transfer) rate constant is unchanged, the termination constant undergoes a considerable reduction. A consideration of the termination reaction as being composed of successive diffusion and chemical processes reveals that the termination of methyl methacrylate is diffusion controlled over the complete range, whereas the slower termination of butyl acrylate is only diffusion controlled at viscosities greater than 15 cp. Both experimental and preliminary theoretical considerations postulate that the diffusion controlled rate constant be proportional to the inverse first power of the solvent viscosity. Unfortunately the experiments performed here were not sufficiently precise as to be able to observe any dependence of the termination rate constant upon the chain length of the radicals involved.

LOS ANGELES, CALIFORNIA

[CONTRIBUTION FROM THE RESEARCH DEPARTMENT, UNION CARBIDE CHEMICALS COMPANY]

The Polymerization of Styrene by n-Butyllithium[1]

BY F. J. WELCH

RECEIVED SEPTEMBER 5, 1958

The rate of polymerization of styrene initiated by n-butyllithium has been studied at temperatures from 20 to 50° in benzene and toluene solution. For n-butyllithium concentrations less than 0.020 M the rate of propagation is proportional to the concentrations of both catalyst and styrene. For higher catalyst concentrations the rate is proportional to the monomer concentration but independent of the catalyst concentration. The degree of polymerization is determined by the ratio of monomer to catalyst. There is no termination reaction, and the rate of initiation is about one-fifth the rate of propagation. The activation energy for propagation is 17 kcal./mole. A polymerization mechanism is proposed to explain these observations.

Introduction

Although there have been many investigations of the kinetics of the cationic polymerization of styrene,[2] the quantitative aspects of the anionic polymerization of this monomer have received little attention. Noteworthy among the few papers on this subject is an excellent study of the kinetics of polymerization in liquid ammonia initiated by potassium amide by Higginson and Wooding.[3] More recently, Korotkov investigated the polymerization of dienes and their copolymerization with styrene in the presence of alkali metal alkyls.[4]

The use of lithium alkyls as catalysts for the polymerization of styrene has been described.[5,6] Although this polymerization proceeds with extreme rapidity in tetrahydrofuran solution,[5] we have found that in hydrocarbon solvents the polymerization is much slower, requiring about 0.5–4.0 hr. for complete conversion at room temperature. In order to learn more about the mechanism of this polymerization, a study of the kinetics of the reaction was undertaken. Since aromatic hydrocarbons are good solvents for both polystyrene and the reactants, benzene and toluene were used as diluents. All of the polymerizations described herein proceeded homogeneously.

Experimental

Materials.—Commercial styrene (Union Carbide Chemicals Company) was distilled at 20 mm. pressure from Linde 5-A Molecular Sieve immediately before use and stored over Molecular Sieve or calcium hydride. Reagent grade benzene or toluene was dried by passing through a column of Molecular Sieve directly into the reaction vessel or by storing over Molecular Sieve or calcium hydride. n-Butyllithium was prepared in 60–80% yields from n-butyl chloride and lithium metal sand in benzene or hexane solution.[7] The lithium chloride was allowed to settle and the clear, supernatant liquid was transferred and stored under nitrogen. The concentration was determined by acid titration.

Molecular Weight Dependence.—All operations were conducted with the rigorous exclusion of air and moisture. The apparatus consisted of a one-liter flask fitted with a stirrer, thermometer and 125-ml. graduated dropping funnel. The top of dropping funnel was connected through a three-way stopcock to flasks containing benzene and styrene, respectively, stored over calcium hydride. The reaction flask and dropping funnel were dried by heating to about 100° at 0.5 mm. pressure. High purity nitrogen was used to break the vacuum. Styrene, 50–100 ml., was transferred to the graduated dropping funnel by applying nitrogen pressure to the styrene reservoir. After determining the volume, it was transferred to the reaction flask. Benzene, 400 ml., was similarly added to the flask. An accurately measured quantity (0.001–0.025 mole) of n-butyllithium solution was added with stirring from a calibrated pipet at room temperature. Polymerization began almost immediately and was essentially complete in 0.5–2.0 hr. External cooling was applied when necessary to keep the temperature below about 70°. Otherwise no attempt was made to control temperature in these runs. The polystyrene was recovered by precipitation in methanol, washed thoroughly with methanol and dried. Yields were quantitative. Intrinsic viscosities were determined in benzene solution at 30°.

Rate Measurements.—Reactants were mixed in a 100-ml., graduated volumetric flask fitted with a stopcock in the

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(1) Presented in part at the 133rd Meeting of the American Chemical Society, San Francisco, April, 1958.

(2) D. C. Pepper, *Quart. Rev.* (*London*), **8**, 114 (1954).

(3) W. C. E. Higginson and N. S. Wooding, *J. Chem. Soc.*, 760 (1952).

(4) A. A. Korotkov, Paper presented at the International Union of Pure and Applied Chemistry Meeting, Prague, Sept., 1957; *Angew. Chem.*, **70**, 85 (1958).

(5) M. Morton, H. L. Stephens and J. L. Hall, Paper presented at the 132nd Meeting of the American Chemical Society, New York, Sept., 1957.

(6) A. Zilkha, M. Albeck and M. Frankel, *J. Chem. Educ.*, **35**, 345 (1958).

(7) T. D. Perrine and H. Rapoport, *Anal. Chem.*, **20**, 635 (1948).

bottom. The flask was dried by heating in a stream of nitrogen. Styrene was added to the flask with a pipet and diluted to the calibration mark with benzene. *n*-Butyllithium was then added. After mixing well, a portion of the mixture was added through the stopcock to a carefully dried, 0.6 × 70 cm. tube that was sealed at the bottom and suspended vertically in a water-bath controlled to ±0.1°. The tube was closed with a rubber stopper. The rate was followed dilatometrically. About 60 sec. elapsed between the time the catalyst was added and the first reading was made.

All polymerizations were followed essentially to completion. When polymerization was complete, the polystyrene produced was recovered and the intrinsic viscosity determined.

Color Intensity Measurement.—Styrene, 10 ml., and variable amounts of *n*-butyllithium were mixed in benzene solution in 50-ml. volumetric flasks. External cooling was applied to remove the heat of polymerization. When polymerization was complete, samples of each of the solutions were transferred under nitrogen to dry, stoppered tubes; and the optical density was determined at 530 mμ using a Beckman Model B spectrophotometer. A 1.0 *M* solution of styrene in benzene was used as the blank. The polystyrene produced was recovered from the remaining solutions and the intrinsic viscosities determined. From the molecular weights of the polystyrene samples the concentration of *n*-butyllithium was calculated.

Results

Molecular Weight Dependence.—Because of the extreme reactivity of lithium alkyls with trace impurities, such as moisture and oxygen, the concentration of *n*-butyllithium was subject to considerable uncertainty in the rate experiments. However, since each molecule of *n*-butyllithium initiates one polymer chain and there is no termination reaction,[5] the effective concentration of *n*-butyllithium may be calculated from the degree of polymerization of the polystyrene produced. In order to use this method for determining the catalyst concentration, the relationship between the intrinsic viscosity and the degree of polymerization calculated from accurately known catalyst concentrations had to be established.

In a series of experiments styrene, 0.9–1.9 *M*, was polymerized at *n*-butyllithium concentrations varying from 0.002 to 0.050 mole/l. Extreme precautions were taken to dry the solvent, monomer and apparatus thoroughly. In Fig. 1 the log of the intrinsic viscosity of polystyrene formed is plotted against the calculated degree of polymerization. The line drawn through the experimental points is that determined using sodium-naphthalene as the catalyst be Szwarc and coworkers.[8] The experimental points deviate from the straight line at high degrees of polymerization corresponding to low catalyst concentrations. This is to be expected since the loss of small quantities of catalyst by reaction with impurities would result in a much greater percentage error at low catalyst concentrations. This relationship is not affected by temperature over the range studied (20–80°). *n*-Butyllithium concentrations quoted in the remainder of this paper have been calculated from the degree of polymerization as measured by the intrinsic viscosity according to the relation in Fig. 1.

Rate of Polymerization.—Figure 2 shows typical first-order plots for the polymerization of styrene in benzene at 20°. For catalyst concentrations less than about 0.020 *M* the rate increases during the first 5–15% of the polymerization and remains constant thereafter. The first-order dependence of the rate of propagation on styrene concentration was observed for initial styrene concentrations as high as 3.7 *M*.

For catalyst concentrations greater than 0.020 *M* the rate deviates from a first-order dependence on styrene concentration. A possible explanation for this will be discussed.

The period of accelerating rate is accompanied by the development of a red-brown color in the originally colorless solution. The color reaches a maximum intensity at the same time that the rate reaches a maximum. This color remains substantially unchanged as long as reactive impurities are excluded. The stability of the color is further evidence for the absence of a termination reaction. The maximum color intensity is proportional to the catalyst concentration, as shown in Fig. 3, and independent of the styrene concentration.

Effect of Catalyst on Rate.—As illustrated in Fig. 4 the rate of propagation is proportional to the concentration of *n*-butyllithium for concentrations less than about 0.020 mole/l. but independent of catalyst for higher concentrations. Temperature in the range 20–45° did not noticeably affect the point at which the break in the curve occurred.

A plot of the log of the rate of propagation for catalyst concentrations less than 0.020 *M* against the reciprocal of the temperature is shown in Fig. 5. From these data an activation energy of 17 kcal./mole and a frequency factor of 10^{11} l./mole/sec. are calculated. A similar activation energy is obtained if the limiting propagation rates at high catalyst concentrations are utilized in the Arrhenius plot. The frequency factor is of the same order of magnitude as the theoretical calculated for second order gas phase reactions.[9]

Discussion

There are several important characteristics of this polymerization that any proposed mechanism must take into account

(1) Initial period of accelerating rate

(2) $R_p = k_p\,(M)(BuLi)$, for $(BuLi) < 0.020\ M$

(3) $R_p = k\,(M)$, for $(BuLi) > 0.020\ M$

(4) $\overline{DP}_n = \dfrac{(M)}{(BuLi)}$

The following simple mechanism which involves the successive additions of lithium alkyl to monomer is consistent with equations 1, 2 and 4.

$$\text{Initiation: } BuLi + M \xrightarrow{k_i} Bu(M)Li \qquad (5)$$

$$\text{Propagation: } Bu(M)_xLi \xrightarrow{k_p} Bu(M)_{x+1}Li \qquad (6)$$

The period of accelerating rate is attributed to the fact that initiation is slower than propagation. It is to be expected that *n*-butyllithium would add to styrene at a different rate than would the resulting product.

The change in dependence of rate on catalyst concentration, equations 2 and 3, suggests that

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[8] R. Waack, A. Rembaum, J. D. Coombes and M. Szwarc, This Journal, **79**, 2026 (1957).

[9] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 72.

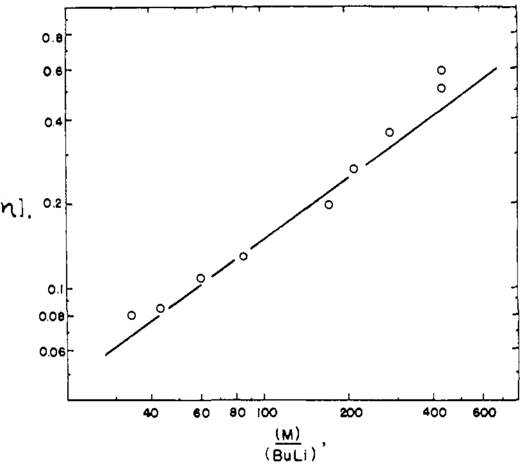

Fig. 1.—Relation of intrinsic viscosity to calculated degree of polymerization. The line drawn through the points is that determined by Szwarc, *et al.*[8]

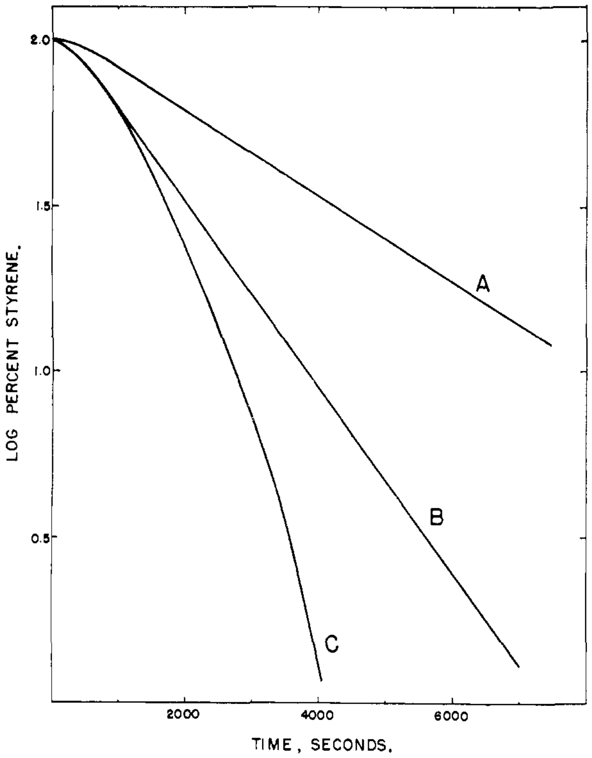

Fig. 2.—Typical polymerization in benzene solution at 20°: (BuLi) is A, 0.004 *M;* B, 0.011 *M;* and C, 0.041 *M.*

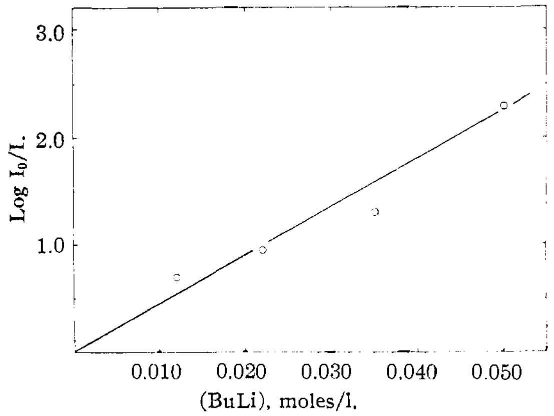

Fig. 3.—Effect of n-butyllithium on the optical density at 530 mμ of the reaction medium at completion of polymerization.

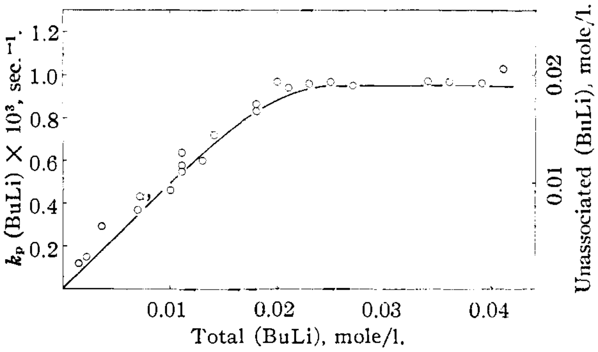

Fig. 4.—Dependence of rate of propagation on the catalyst concentration. The line is the calculated relation between unassociated (BuLi) and total (BuLi) assuming m = 7 and K = 10^{11} in eq. 7.

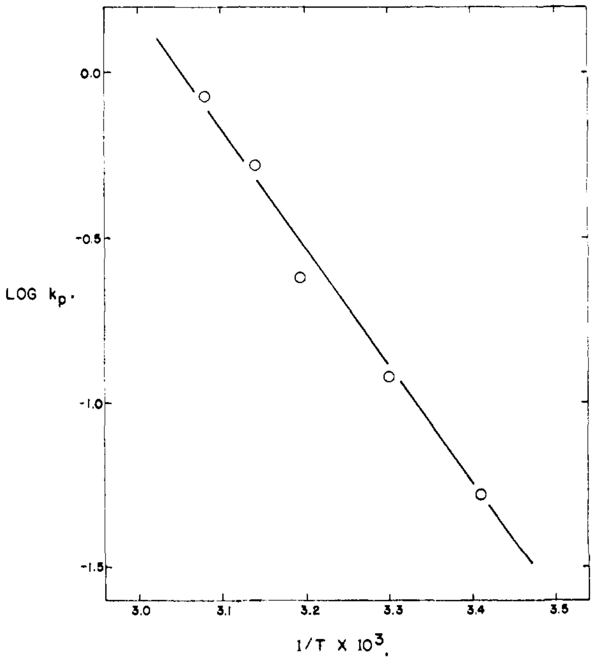

Fig. 5.—Arrhenius plot for propagation.

above a critical concentration, only part of the lithium alkyl present is active in the polymerization. Since it is known that lithium alkyls are highly associated in solution,[10] it appears reasonable to assume that associated lithium alkyls are inactive in the polymerization and 0.020 M represents the critical concentration for association in benzene solution. Therefore, in addition to the initiation and propagation reactions described above, an association equilibrium must be considered in the mechanism and it must be assumed

$$\text{Association: } m\text{RLi} \overset{K}{\rightleftarrows} (\text{RLi})_m \qquad (7)$$

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[10] G. E. Coates, "Organo-Metallic Compounds," Methuen and Co., London, 1956, p. 7; T. L. Brown and M. T. Rogers, THIS JOURNAL, **79**, 1858 (1957).

that only the unassociated lithium alkyls are catalytically active.

If values for m and K are known, the concentration of unassociated RLi present for particular total catalyst concentrations may be calculated.[11] The degree of association of *n*-butyllithium in benzene solution has been reported to be about 5–7.[10] By choosing a value of $m = 7$ and a value for K such that a critical concentration for association of about 0.02 M resulted, the solid curve drawn in Fig. 4 was calculated. The value for K which gave this close fit with the experimental data was 10.[11] Such a value for the equilibrium constant seems reasonable since it corresponds to $-\Delta F = 15$ kcal./mole which is about the value to be expected for the energy of such an association reaction. Although other values for m and K might give satisfactory agreement with the experimental data, the ones chosen are reasonable and demonstrate the plausibility of this treatment.

The fact that there is no break in the curve in Fig. 1 corresponding to the break observed in Fig. 4 indicates that even associated butyllithium initiates growing polymer chains, although it does not contribute to the rate of polymerization. This requires that the equilibrium (eq. 7) be established rapidly and involve the growing polymer chains, $Bu(M)_xLi$, as well as *n*-butyllithium. When the lithium alkyl is associated, it is assumed to be in a dormant state; but when it is unassociated it participates in the propagation reaction.

Although it is doubtful that *n*-butyllithium is ionized to an appreciable extent, the color developed during the polymerization is evidence for the formation of α-alkylbenzyl anions, which are probably present in the hydrocarbon solution as ion pairs. Since there is no apparent change in the dependence of color intensity on catalyst concentration at 0.020 M butyllithium in Fig. 3, association of $Bu(M)_xLi$ does not affect its absorption of light.

From the shape of the rate curves, Fig. 2, it is estimated that $k_p = 5k_i$. Although it might appear that a mechanism of the type proposed involving an initiation step that is slower than propagation would lead to a broad molecular weight distribution, the calculations of Gold[12] indicate that such is not the case. For the case where $k_p/k_i = 10$, the ratio of weight to number average molecular weights is never greater than 1.35 even at very low conversions. For degrees of polymerization of 50 and 500 the calculated ratios are 1.06 and 1.00, respectively.

It has been assumed that m and K are independent of the substituent R in the lithium alkyl. However, the fact that the rate of propagation deviates slightly from a first-order dependence on monomer at high catalyst concentrations (Fig. 2) may be an indication that this assumption is not entirely true. A slight decrease in the value of either m or K as R increases in size would result in the formation of more unassociated lithium alkyl and hence a faster rate. This could happen only for catalyst concentrations in excess of about 0.02 M since at lower concentrations all of the lithium alkyl is already unassociated.

The rate of polymerization is accelerated markedly by the addition of small quantities of ethers, tertiary amines and the like. Tetrahydrofuran is particularly effective in this respect. A later paper will discuss the effect of such substances on the rate of polymerization.

Acknowledgments.—The author is greatly indebted to Messrs. P. D. Wills, H. J. Paxton and P. E. Peters for assistance in the experimental work and to Dr. R. D. Lundberg for many helpful discussions.

(11) A. E. Alexander and P. Johnson, "Colloid Science," Vol. II, Oxford University Press, London, 1949, p. 672.

(12) L. Gold, *J. Chem. Phys.*, **28**, 91 (1958).

SOUTH CHARLESTON, WEST VIRGINIA

[CONTRIBUTION FROM THE GRADUATE DEPARTMENT OF APPLIED SCIENCE, UNIVERSITY OF CINCINNATI]

The Fluorescence of Some Coumarins[1]

BY CHARLES E. WHEELOCK[2]

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In a study of the effect of constitution on the fluorescence of coumarins, the ultraviolet absorption, fluorescence intensity at various concentrations in alcohol, fluorescence spectra and stability of fluorescence intensity in alkaline solution have been determined. The effect of substituents on intensity of fluorescence and on position of the fluorescence band maximum was noted. Concentration quenching and ultraviolet absorption were found to be related. Structures hindering cleavage of the heterocyclic ring by alkaline solution stabilize fluorescence.

In earlier studies, the effect of substituents on the intensity of fluorescence of coumarins was studied by visual observation of solutions in sunlight.[3–5] As the fluorescence intensities of solutions vary irregularly with concentration,[6,7] comparison of coumarins at a single concentration is inadequate. Consequently, the behavior of selected coumarins in solutions of various concentrations as well as the wave lengths of their absorption and emission bands is of interest in further clarification of the effects of structure on the fluorescence of coumarins. As electron attracting groups in the 3-position and electron repelling groups in the 7-

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(1) Taken from a thesis submitted by Charles E. Wheelock in partial fulfillment of the requirements for the D.Sc. degree, University of Cincinnati, 1947. This work was sponsored by the Procter and Gamble Co.

(2) The Phillips Petroleum Co., Bartlesville, Okla.

(3) S. Rangaswami and T. R. Seshadri, *Proc. Ind. Acad. Sci.*, **12A**, 375 (1940).

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