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The Polymerization of Heteroaromatic Monomers

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ABSTRACT

Vinyl monomers containing a heteroaromatic substituent such as thiophene, thiazole, oxazole, and pyridine have been synthesized and radical copolymerization with styrene of these monomers was studied. Monomer reactivity ratios (r_1 , r_2) and Alfrey-Price $Q-e$ values were determined. The reactivities of these monomers ($1/r_1$) are generally related to localization energy of the β -carbon of monomers (L_β). In the case of anionic polymerization of isopropenyl monomers, a considerable amount of monomer remained in the living polymerization system. The equilibrium monomer concentrations were determined at different temperatures, and the heats and entropies of polymerization

were obtained. We also obtained propagation rates for these monomers by the capillary flow method. The effect of heteroaromatic compounds on the polymerization of styrene in THF initiated by the sodium salt of α -methylstyrene was studied.

INTRODUCTION

Szwarc and his co-workers carried out an extensive kinetic study of living polymerization. Few papers have appeared dealing with the living anionic polymerization of vinyl or isopropenyl monomers containing a heteroaromatic substituent except for that regarding 2-vinyl pyridine. Vinyl or isopropenyl monomers having an aromatic heterocycle such as oxazole, thiazole, and pyridine are thought to be very similar to styrene both with respect to the structure and electronic properties, since they possess a cyclic structure with a stable 6- π electron conjugation system like benzene. Therefore, it was expected that these monomers would give living polymers under appropriate conditions. From these viewpoints, a systematic study of the polymerization of such monomers has become of special interest to us. First of all, radical copolymerization of heteroaromatic monomers with styrene was carried out partly for the purpose of comparing polymerization behaviors of radical and anionic polymerization.

RADICAL COPOLYMERIZATION WITH STYRENE

Radical copolymerization of heteroaromatic monomers (M_2) with styrene (M_1) was carried out by the conventional method. The conversion was always controlled within 10%, and the copolymer compositions were determined by elemental analysis. Monomer reactivity ratios r_1 and r_2 were determined both by the Finemann-Ross and the Mayo-Lewis methods, and the Alfrey-Price's Q and e values were calculated from them. The values are summarized in Table 1 together with those of the monomers reported in the literature.

It is convenient to compare the monomer reactivity by $1/r_1$ since it stands for the relative rate of the addition of the monomer to benzyl radical. From Table 1, it is evident that all the heteroaromatic monomers tried are more reactive than styrene since $1/r_1$ is always larger than unity. Moreover, monomers with two heteroatoms are always more reactive than those with one heteroatom except for 3-isopropenyl-5-methylisoxazole, e.g., all

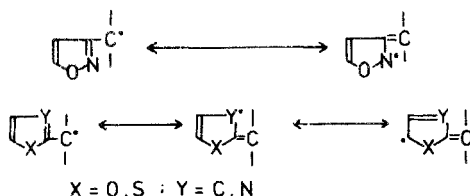
TABLE 1. Monomer Reactivity Ratios and Alfrey-Price's Q and e Values

No.	Monomer (M_2)	r_1	r_2	Q	e	$1/r_1$
	2-Vinyl furan [6]	0.24	1.9	1.9	-0.8	4.2
	2-Vinyl thiophene [7]	0.35	3.1	3.0	-0.8	2.9
	2-Vinyl pyridine [8]	0.55	1.1	1.1	-0.1	1.8
	2-Isopropenylpyridine	0.42	0.95	1.1	+0.16	2.4
I-2	2-Vinyl-4,5-dimethylloxazole	0.18	1.3	2.2	+0.40	5.6
I-3	2-Isopropenyl-4,5-dimethylloxazole	0.15	2.2	2.8	+0.24	6.7
I-4	2-Vinyl-4-isobutyl-5-methylloxazole	0.10	3.0	4.2	+0.30	10
I-5	2-Isopropenyl-4-isobutyl-5-methylloxazole	0.10	3.4	4.1	+0.24	10
II-1	2-Vinyl thiazole [3]	0.14	3.3	3.5	+0.08	7.1
II-2	2-Isopropenylthiazole	0.09	3.8	4.8	+0.24	11
II-3	2-Vinyl-4-methylthiazole	0.15	2.8	3.2	+0.13	6.7
III-2	3-Isopropenyl-5-methylisoxazole	0.67	0.98	0.88	-0.15	1.5
III-1	2-Isopropenyl-5-methyl-1,3,4-oxadiazole	0.16	0.83	2.0	+0.62	6.2

oxazole monomers are more reactive than furan or pyridine monomers, and thiazole monomers are also more reactive than thiophene or pyridine monomers. Koton studied the polymerization rates of vinyl compounds containing furan, thiophene, and pyridine, and concluded that the polymerizabilities of these monomers increased by the introduction of a heteroatom into the ring or by the addition of condensed ring [1]. It was further reported that in the series styrene, 2-vinyl pyridine, 2-vinyl quinoline, and 4-vinyl pyridine, the reactivities increased from 1.00 to 1.82 to 2.04 to 5.88 [2]. From this fact it was concluded that the introduction of a second heteroatom further enhanced the reactivity of the monomer.

These empirical generalizations are quite consistent with the tendency found here, and they can be extended to the oxazole and the thiazole monomers.

The reactivity of 3-isopropenyl-5-methylisoxazole turned out to have a different trend from the others. This may be due to the poorer conjugation of the isoxazole ring compared to the other heteroaromatics, since, in the former compound, heteroatoms locate adjacent to each other and prevent the radical from delocalizing throughout the ring. The difference is clearly shown by the number of the contributing structures.



A similar explanation was given for the different reactivities of 2-vinyl- and 4-vinylthiazoles by Schilling et al. [3]. The different trend of the isoxazole monomer is also reflected in their Q and e values. The e values of all the other monomers listed in Table 1 are larger than that of styrene, i.e., -0.8 , showing the electron-withdrawing nature of such rings. The introduction of a second heteroatom to the ring apparently increased the positive character of double bond.

The polymerizabilities of vinyl monomers have been investigated from the theoretical viewpoint and were explained in terms of the localization energy [4] or the resonance stabilization energy (ΔE_{rs}) between the attacking radical and the monomer [5]. The author

calculated the energy levels of the molecular orbitals of each monomer and those of the radical derived from it by the simple Hückel method. The parameters of heteroatoms used in the calculations are shown in Table 2. Values of L (localization energy of β -carbon) are shown in Table 3. In Fig. 1, $\log(1/r_1)$ is plotted

TABLE 2. Parameters Used in the Molecular Orbital Calculations [9]

Heteroatom (X)	a	b	l
-O-	2	0.2	0.6
-N-	0.6	0.1	1
-S-	0	0	0.5
-CH ₃	3	-0.1	1

$\alpha_X^a = \alpha + a\beta$, α_X : Coulomb integral of heteroatom X. $\alpha_{adj} = \alpha + b\beta$, α_{adj} : Coulomb integral of carbon adjacent to X. $\beta_{c-x} = 1\beta$, β_{c-x} : Exchange integral between carbon and X.

TABLE 3. Relative Monomer Reactivities and Localization Energies

No.	Monomer (M ₂)	1/r ₁	L(- β)
1.	Styrene	1.00	1.70
2.	2-Vinyl pyridine	1.8	1.69
3.	2-Vinyl thiophene	2.9	1.61
4.	2-Vinyl furan	4.2	1.57
5.	2-Vinyl-4, 5-dimethyloxazole	5.6	1.53
6.	2-Vinyl-4-methylthiazole	6.7	1.55
7.	2-Vinyl thiazole	7.1	1.58
8.	2-Vinyl-4-isobutyl-5-methyloxazole	10	1.55

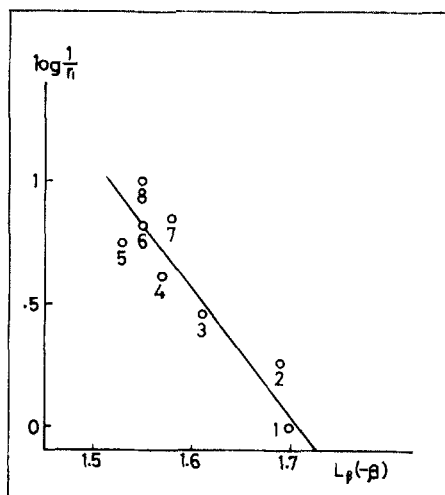


FIG. 1. $\log (1/r_1)$ vs $L_{\beta}(-\beta)$.

against L_{β} . Figure 1 shows that the reactivities of these monomers are generally related to L_{β} and that the monomer reactivity increases in the decreasing order of L_{β} . Although the relation is rather rough, it is thought to be satisfactory for the qualitative discussion taking into account that many assumptions have been made in the orbital calculations, and that $1/r_1$ has been taken as a parameter for the monomer reactivity. Thus empirical generalizations, 1) the introduction of a heteroatom into the ring enhances the monomer reactivity, and 2) a second heteroatom further enhances the reactivity, are supported from the theoretical standpoint.

KINETICS OF ANIONIC POLYMERIZATION OF HETEROAROMATIC MONOMERS BY THE CAPILLARY FLOW METHOD

The anionic polymerization in THF of various heteroaromatic vinyl and isopropenyl monomers was accomplished by a use of sodium naphthalene as an initiator. All monomers but furan monomers gave living polymers.

Anionic polymerization is generally too rapid for the measurement of its polymerization rate by the method employing a sampling

technique. We therefore applied the capillary flow method which was used for the investigation of anionic polymerization by Szwarc [10]. The apparatus used in this study is shown in Fig. 2.

Two cylindrical reservoirs contained the solution of sodium naphthalene and of the monomer respectively. The capillary was immersed in a beaker containing methanol. The solution from each reservoir was pressured into the capillary by dry and purified argon. The conversion to polymer was determined by gas chromatography to estimate the concentration of the residual monomer using *o*-xylene as an internal standard.

A typical time-conversion curve and the first-order kinetic treatment are shown in Fig. 3.

In some cases of isopropenyl monomers, conversion curves were saturated and never reached 100%. In these cases the propagation constant K_p was determined by the slope of the tangent line at the origin in the conversion curve. The propagation rate constants of heteroaromatic monomers are summarized in Table 4.

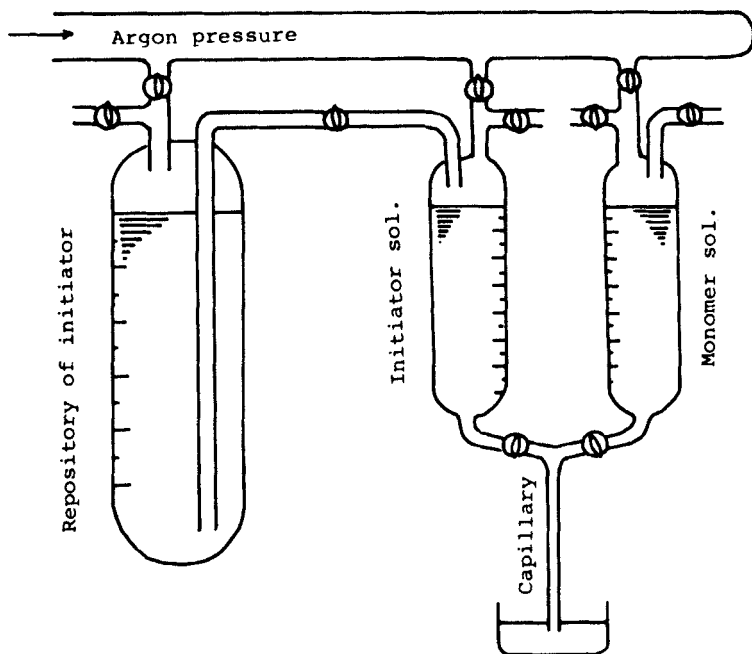


FIG. 2. Apparatus of the capillary flow method for measuring rates of fast reactions.

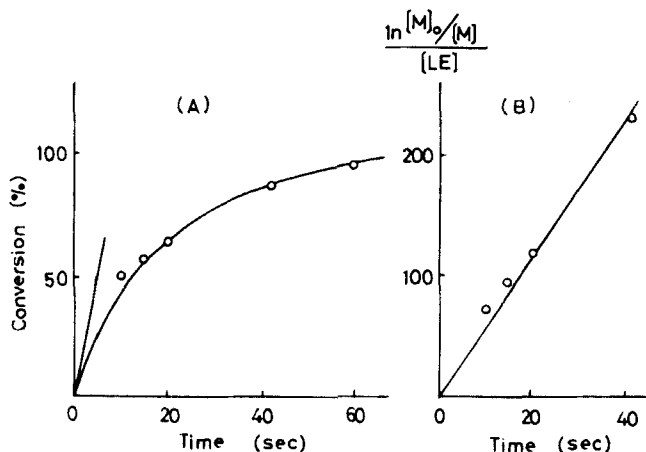
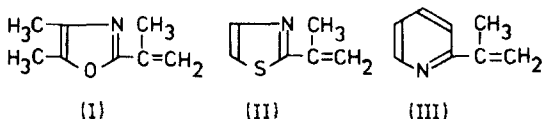


FIG. 3. Polymerization of 2-vinylthiophene at 25°C. (A) Conversion curve. (B) Rate of polymerization. $[LE] = 0.90 \times 10^{-2}$ mole/liter; $[M]_0 = 7.3 \times 10^{-2}$ mole/liter.

EQUILIBRIUM ANIONIC POLYMERIZATION OF ISOPROPENYL MONOMERS CONTAINING AROMATIC HETEROCYCLES

In this article, the anionic polymerization of 2-isopropenyl-4,5-dimethyloxazole (I), 2-isopropenylthiazole (II), and 2-isopropenylpyridine (III) in THF are described.



These monomers produced red colored living polymers after the addition of sodium naphthalene as an initiator. It was observed, however, that a considerable amount of monomer remained in the polymerization system at room temperature in each case. The conversion of the monomer into polymer increased at lower temperatures. Such phenomena are well known in the case of α -methylstyrene and are interpreted as equilibrium polymerization.

TABLE 4. Polymerization Rate Constants Measured by the Capillary Flow Technique

Monomer	$[LE] \times 10^2$ (mole/liter)	k_p [liter/(mole)(sec)]
Styrene	0.53	510
2-Vinyl thiophene	0.90	6
2-Vinyl pyridine	0.63	3560
2-Isopropenylpyridine	1.29	60
2-Vinyl-4, 5-dimethylloxazole	0.76	4.8×10^5
2-Isopropenyl-4, 5-dimethylloxazole	0.86	700
2-Vinyl-4-methylthiazole	0.42	5600
2-Vinyl-4, 5-dimethylthiazole	0.90	9850
2-Isopropenylthiazole	0.81	240
2-Isopropenyl-4-methylthiazole	1.00	770
2-Isopropenyl-4, 5-dimethylthiazole	0.52	1560
2-Isopropenyl-5-methyl-1, 3, 4-oxadiazole	0.90	340

The equilibrium polymerization of α -methylstyrene has been extensively studied by McCormick [11], Bywater [12], and Szwarc [13]. The relation between the equilibrium monomer concentration, M_e , and the equilibrium constant, K_∞ , was given by Tobolsky [14] as shown in Eq. (1), assuming that the equilibrium constant K_n in Eq. (2) is independent of n :

$$(M_0 - M_e)/P_{\text{total}}^* = K_\infty M_e / (1 - K_\infty M_e) \quad (1)$$



where P_{total}^* , M_0 , and P_n^* denote the total living end concentration, initial monomer concentration, and living n -mer concentration, respectively. Szwarc modified Eq. (1) and obtained the more general expression (3) [15] which is applicable to the system in which the equalities $K_n = K_{n+1}$ are assumed to be valid only for n exceeding some value $s + 1$ ($s > 1$), whereas for $n \leq s$ the respective K_n 's may differ from K_∞ and from each other:

$$(M_0 - R_s - M_e)/P_{\text{total}}^* - Q_s^* = K_\infty M_e (1 - K_\infty M_e) \quad (3)$$

where Q_s^* and R_s denote the concentration of living polymers which have a degree of polymerization less than s and the amount per unit volume of the monomer incorporated in these polymers, respectively.

For a high number-average degree of polymerization, the approximation $K_\infty = 1/M_e$ is obtained both from Eqs. (1) and (3). Thus the determination of the temperature dependence of the equilibrium constant is reduced to the analytical problem of measuring the equilibrium monomer concentrations at different temperatures. McCormick [11], Bywater [12], and Szwarc [13] independently measured the residual monomer concentration of α -methylstyrene in equilibrium with its living polymer. Bywater also studied the styrene-living polystyrene system [16]. In the latter case, the polymerization was carried out in benzene or cyclohexane rather than THF, and n -butyllithium was used as initiator to avoid side reactions since the residual concentration of styrene proved to

be much lower compared to α -methylstyrene. A higher temperature (100 to 150°C) was required to measure the equilibrium monomer concentration even by the use of UV spectroscopy for analyses.

With respect to the monomers studied here, the equilibrium monomer concentrations were comparatively high and could be determined by gas chromatography using an internal or external standard.

2-Isopropenyl-4, 5-dimethyloxazole (I) was polymerized using sodium naphthalene or living α -methylstyrene tetramer as initiator. The experiments were carried out under three different initial conditions to check the reproducibility of the data. The results are shown in Table 5.

Approximating $K_{\infty} = 1/M_e$, the thermodynamic equation for polymerization is expressed as

$$\ln(1/M_e) = -\Delta H/RT + \Delta S^{\circ}/R \quad (4)$$

where ΔH , ΔS° , and R denote the heat and the entropy of polymerization and gas constant, respectively. In Fig. 4, $\ln(1/M_e)$ is plotted

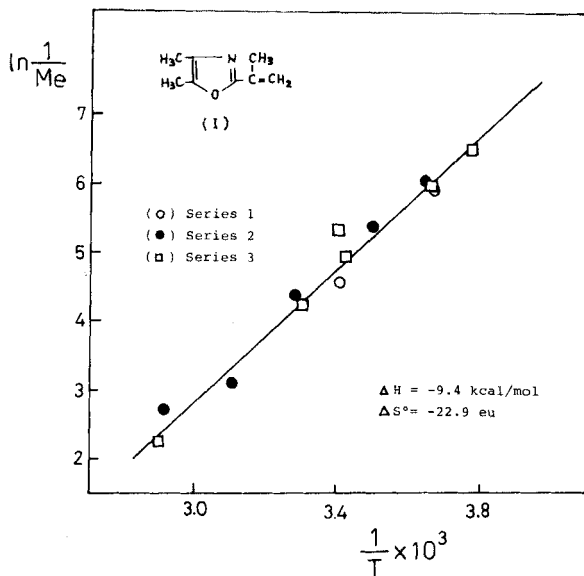


FIG. 4. Plot of $\ln(1/M_e)$ vs $1/T$ for Monomer I.

TABLE 5. Equilibrium Monomer Concentration of (I) at Different Temperatures

Series ^a	Temperature (°K)	Time (hr)	[LE] (mole/liter)	[M ₀] (mole/liter)	[M _e] (mole/liter)
1	273.9	65	0.0046	0.20	0.0026
	286.1	65	0.0046	0.20	0.0049
	304.7	65	0.0046	0.20	0.0133
	323.1	65	0.0046	0.20	0.0471
	343.1	65	0.0046	0.20	0.0630
2	273.5	65	0.0058	0.15	0.0029
	293.2	65	0.0058	0.15	0.0104
3	265.2	65	0.0098	0.73	0.0016
	273.5	65	0.0098	0.73	0.0028
	292.2	65	0.0098	0.73	0.0067
	294.4	65	0.0098	0.73	0.0046
	303.2	65	0.0098	0.73	0.0146
	343.2	65	0.0098	0.73	0.1030

^aSeries 1 and 2 were initiated by living α -methylstyrene tetramer, while series 3 was initiated by sodium naphthalene.

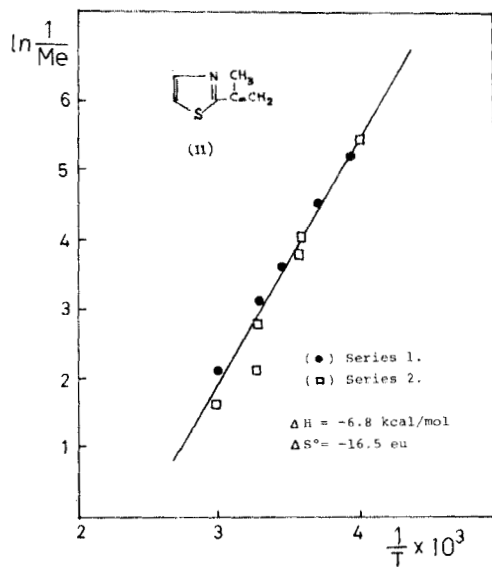
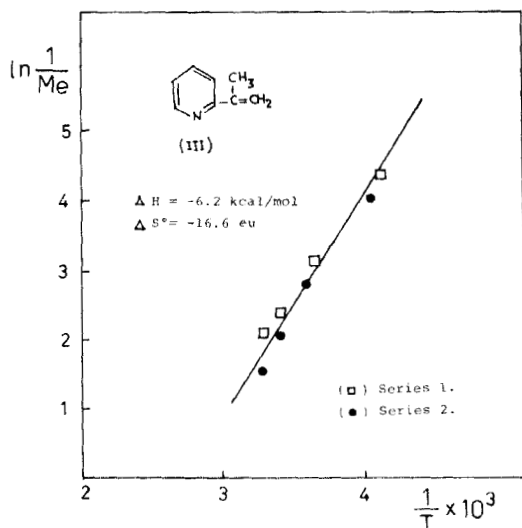
against the reciprocal of temperatures ($^{\circ}\text{K}$). The data obtained from three series of experiments gave a consistent straight line, suggesting that Eq. (4) is valid for the temperature range of the experiments, i.e., equilibrium polymerization occurred. The slope of the line and the intercept on the y-axis were calculated by the least squares method, and from their values ΔH and ΔS° were obtained as -9.4 kcal/mole and -22.9 eu, respectively.

Alternatively, by substituting -9.4 kcal/mole for ΔH in Eq. (4), ΔS° can be calculated for each plot. The results are shown in Table 6. Table 6 shows that the constancy of ΔS° is excellent throughout the three experimental series. The values calculated in this way are in good agreement with those calculated by the intercept.

The same procedures were carried out with respect to the monomers II and III, and the results are shown in Figs. 5 and 6. In all cases, a linear relation was obtained between $\ln(1/M_e)$ and $1/T$.

TABLE 6. S° Calculated from the Slope and K_{∞} . Monomer (I)

Series	Temperature ($^{\circ}\text{K}$)	K_{∞} (liter/mole)	ΔS° (eu)
1	273.9	385	-22.5
	286.1	204	-22.3
	304.7	75.2	-22.2
	323.1	21.2	-23.1
	343.1	15.9	-21.9
2	273.5	345	-22.8
	293.2	96.2	-23.0
3	265.2	625	-22.6
	273.5	357	-22.7
	292.2	149	-22.2
	294.4	217	-21.3
	303.2	68.5	-22.6
	343.2	9.71	-22.8

FIG. 5. Plot of $\ln(1/Me)$ vs $1/T$ for Monomer II.FIG. 6. Plot of $\ln(1/Me)$ vs $1/T$ for Monomer III.

From Figs. 5 and 6, ΔH and ΔS° were obtained in the same manner as in the case of monomer I. Those values are summarized in Table 7 along with those of other monomers reported in the literature.

Table 7 shows that the values obtained for monomers I, II, and III are close to those for α -methylstyrene. The marked difference in ΔH between α -methylstyrene and styrene was explained by the steric hindrance exerted by the α -methyl substitution [17]. Steric hindrance is common to monomers I, II, and III, and their values for the heats of polymerization appear reasonable. Their entropies of polymerization are a little smaller than that of α -methylstyrene.

At room temperature, α -methylstyrene gives only low molecular weight oligomers, the concentrated solution of which gives only a precipitate when it is poured into a large volume of methanol. On the other hand, monomers I, II, and III gave powdery polymers even at room temperature, showing that their anionic polymerizabilities are better than that of α -methylstyrene. This conclusion was supported by their ceiling temperatures as shown in Table 7.

TABLE 7. Heats and Entropies of Polymerization and Ceiling Temperatures.

Monomer	ΔH_{ss} (kcal/mole)	ΔS_{ss}° (eu)	T_c^a (°C)	Ref.
I	-9.4	-22.9	137	
II	-6.8	-16.5	139	
III	-6.2	-16.6	100	
α -Methylstyrene	-6.96	-24.8	8	11
	-8.02	-28.75	6	12
	-7.47	-26.5	9	13
Styrene	-17.2	-28.7	326	16
Methyl methacrylate	-12.9	-29.5	164	25
Isobutyraldehyde	-3.7	-17.6	-63.4	26
Chloral	-3.5	-12.4	11	26

^a T_c is defined by $\Delta H/\Delta S^\circ$.

At temperatures higher than 60°C, some side reaction other than polymerization-depolymerization seems to take place slowly in the polymerization of monomers II and III, since the plots obtained from the sample, which was maintained at 60°C for many hours and then allowed to stand at room temperature for enough time to restore the equilibrium before killing the living ends, deviated considerably from the plot for a sample which was polymerized at room temperature from the first. Polymerization occurred much faster than the side reaction, however, and the system attained its equilibrium before the side reaction became appreciable, at least at temperatures lower than 60°C.

ANIONIC POLYMERIZATION OF STYRENE IN THE PRESENCE OF PYRIDINE

Some papers have been published regarding the effect of additives on the rates of anionic polymerization of styrene [18, 19]. Welch reported [20] that the rate of polymerization of styrene initiated by *n*-butyllithium in benzene was greatly accelerated by small quantities of Lewis bases, such as ethers or amines, and retarded by Lewis acids, such as zinc or aluminum alkyls. In general, the marked increase in polymerization rate by Lewis bases is explained to be due to the complex formation of the type $R^-[Li\ 2B]$, resulting from the activation of the carbanion. On the other hand, Lewis acids form complexes of the type $[RA]^-Li^+$ as a result of the deactivation of the carbanion.

Szwarc reported [21] the polymerization of styrene in THF in the presence of anthracene, which formed a complex with living polystyrene and greatly retarded the polymerization rate. In this case, polymerization proceeded to completion, and the living polymer complexed with anthracene was called a "dormant polymers" because it had a potential ability to grow. The effect of glymes were also reported by Szwarc and his co-worker [22].

In this paper we report the marked effect of pyridine for decreasing the polymerization rate of styrene in THF initiated by the sodium salt of α -methylstyrene tetramer. When a THF solution of styrene with a small quantity of pyridine as an additive was mixed with the initiator, the red color of the initiator immediately disappeared and a yellow color developed. Polymerization proceeded gradually, and finally all the monomer was consumed. Without any additive, the anionic polymerization of styrene in THF is a very fast process, and a skillful technique is required to determine its rate. In the presence of pyridine, however, the

polymerization rate decreased so much that it could be determined by the simple method described in the experimental section. Polymerization obeyed a simple first-order rate equation:

$$\ln[M]_0/[M] = k_p[LE]t \quad (5)$$

Plots of $\log[M]_0/[M]$ against time, shown in Fig. 7, resulted in a straight line passing through the origin.

From the slope of the line a, k_p (apparent) was calculated to be $0.19 \text{ mole}^{-1} \text{ liter sec}^{-1}$, which was very much smaller than that in the absence of pyridine. In the case of line a, pyridine was first mixed with the initiator and then monomer solution was added to this mixture. On the other hand, in the case of the line b, pyridine

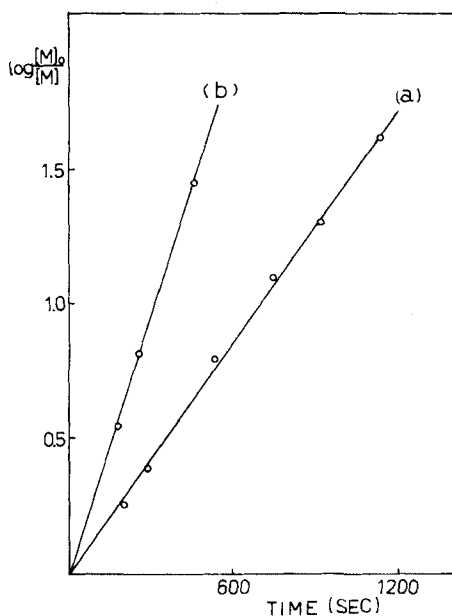


FIG. 7. Plots of $\log([M]_0/[M])$ vs time. Polymerization conditions: (a) $[LE] = 0.019 \text{ mole/liter}$, $[Py]/[LE] = 3$, $[M]_0 = 0.65 \text{ mole/liter}$; (b) $[LE] = 0.018 \text{ mole/liter}$, $[Py]/[LE] = 2$, $[M]_0 = 0.65 \text{ mole/liter}$. Initiator: Na^+ , $(\alpha\text{-MeSt})_4^{2-}$, Na^+ in both cases. Methods of mixing: (a) (pyridine + initiator) + monomer; (b) (pyridine + monomer) + initiator.

TABLE 8. Molecular Weights of Polystyrenes Obtained in the Presence of Pyridine

Run	[LE] (mole/liter)	$\frac{[M]_0}{[LE]}$	$\frac{[Py]^a}{[LE]}$	$[\eta]^b$	MW, obs ^c	MW, calc ^d	Method ^e
1	0.11	10	14	0.047	-	-	Argon
2	0.096	15	21	0.072	-	-	Argon
3	0.018	42	28	0.097	9800	8900	Vacuum
4	0.018	43	55	0.098	9800	9100	Vacuum
5	0.048	60	83	0.124	15000	13000	Argon
6	0.029	97	14	0.140	18000	20000	Argon
7	0.015	194	28	0.230	35000	40000	Argon

^aPy: Pyridine.

^bMeasured in benzene at 30°C.

^cCalculated from the relation, $[\eta] = 1.0 \times 10^{-4} [M]^{0.74}$.

^dCalculated by $MW = 2[M]_0/[LE] \times 104 + 470$. Initiator: $Na^+(\alpha\text{-MeSt})_4^{2-}, Na^+$.

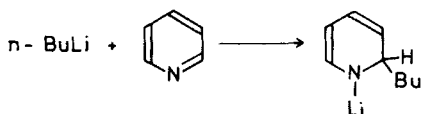
was first mixed with monomer and the mixture was added to the initiator. In the latter case the line also passed through the origin, indicating that the complex formation of carbanion with pyridine was much faster than polymerization.

The intrinsic viscosities of the polystyrene prepared in the presence of pyridine are shown in Table 8.

Table 8 shows that intrinsic viscosities increased in parallel with the ratio of initial monomer concentration to that of living ends, i.e., $[M]_0/[LE]$. The molecular weights of the polymers calculated from the intrinsic viscosities are compared to those calculated on the assumption of typical living polymerization (Table 8, MW columns). Both values are approximately the same, showing that no significant chain transfer or termination had occurred during the polymerization process. Thus it was concluded that pyridine had a marked effect on the polymerization rate but not on the molecular weight of the polymer. This system is thought to be an example of dormant polymers.

Changes in the electronic spectrum are shown in Fig. 8. On addition of pyridine to living polystyrene in THF, the absorbance at 340 nm diminished at once, indicating that a drastic change had occurred at the living ends.

It was reported that *n*-butyllithium formed a σ -complex with pyridine [23]:



The structure of the complex was confirmed by its NMR spectrum. Considering this fact and the drastic decrease of the absorbance at 340 nm, the complex between living polystyrene and pyridine may be close to a σ -complex, which does not have absorption at wavelengths longer than 300 nm. The remaining weak absorption may be due to the polymerization of the active species. However, since the absorption maximum shifted from 340 to 330 nm, pyridine must have some weak interaction with this species. Accordingly, we consider that pyridine has two types of interaction with living polystyrene. The nature of the complex is not yet clear, and further study is now in progress.

We have recently shown that dipyridyls are formed in the reaction of the sodium salt of α -methylstyrene tetramer with pyridine [24]. In the case of the reaction of living polystyrene

which indicates that the reactivities of the carbanions are greatly affected by the substituents.

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