of cyclic oxonium and the nucleophilicity of monomer. The entropy factor is also important. The results of the present study have shown that the nucleophilicity of monomer which varies very little depending on the monomer ring size is not a determining factor in the big difference of the propagation rate constant between the tetrahydrofuran and oxepane polymerizations.

In the consideration of the mechanism of the propagation, the values of activation parameters of the propagation in the polymerizations of four-, five-, and seven-membered cyclic ethers (Table IV) are quite informative. It is seen that the rate is controlled by complicated combinations of the activation enthalpy and entropy. It is of interest to note that the activation enthalpy of the propagation of a more strained monomer of oxetane (as is seen from ΔH_s[12] in Table IV) is higher than that of a less strained monomer of tetrahydrofuran. Also, the propagation rate constant of oxepane, which is more strained than tetrahydrofuran,[5] is smaller than that of tetrahydrofuran. Thus, the strain in the cyclic ether monomer is not related to the activation enthalpy of propagation. The results of the kinetic analysis in the polymerizations of a series of cyclic ethers have clearly shown that an element of the activation entropy is very important for governing the rate of propagation.[6] The activation entropy may possibly be determined by the solvation (initial state)-desolvation (transition state) phenomena as well as the spatial orientations of the electrophile (the propagating species of cyclic oxonium structure) and the nucleophile (the monomer) in the transition state.[13]

Very recently, it has been reported[14] that the tetrahydrofuran polymerization proceeds *via* two species, *e.g.*, the free ion and the ion pair. However, the contribution of the free ion to the overall k_p is not so large that the over all k_p obtained previously by us seems to permit the above discussion of reactivity. Studies on the reactivity of cyclic oxonium species are necessary for the full understanding of the propagation of the cationic polymerization of cyclic ethers.

[12] F. S. Dainton, T. R. E. Devlin, and P. A. Small, *Trans. Faraday Soc.*, 51, 1710 (1955).

[13] T. Saegusa, S. Matsumoto, M. Motoi, and H. Fujii, *Macromolecules*, 5, 236 (1972).

[14] J. M. Sangster and D. J. Worsfold, *Macromolecules*, 5, 229 (1972).

Free-Radical Polymerization of 1-Ferrocenyl-1,3-butadiene and 1-Phenyl-1,3-butadiene. Reactivity Ratios and *Q* and *e* Values

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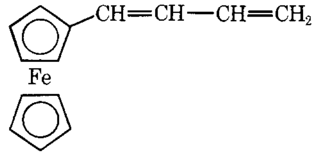
ABSTRACT: The monomers 1-ferrocenyl-1,3-butadiene (1) and 1-phenyl-1,3-butadiene (2) have been synthesized and their characteristics in homopolymerization reactions and in copolymerization reactions with styrene have been investigated. Glpc and elemental analysis data have been used to calculate polymerization rates, reactivity ratios, and *Q* and *e* values for monomers 1 and 2. For the styrene–butadienylferrocene system, $r_1 = 0.76 \pm 0.01$, $r_2 = 2.47 \pm 0.01$, ($Q = 1.56$, $e = -0.80$); for the styrene–butadienylbenzene system, $r_1 = 0.71 \pm 0.01$, $r_2 = 1.20 \pm 0.01$ ($Q = 1.49$, $e = -0.79$). Low molecular weight polymers were obtained in all cases. For the styrene–butadienylferrocene system, $\bar{M}_n$ ranged from 1300 to 1950; for the styrene–butadienylbenzene system, $\bar{M}_n$ ranged from 1700 to 3800.

Many polymers that contain the ferrocene nucleus have been prepared and studied in recent years and these have been reviewed recently.[1] These polymers are of interest because of their potential electrical and magnetic properties, their catalytic activity, and their redox properties, to mention only a few. In many polymer applications, a controlled amount of cross-linking of polymer chains is desirable after the polymer forming reaction has been accomplished. The monomers, 1-ferrocenyl-1,3-butadiene (1) and 1-phenyl-1,3-butadiene (2), thus have the potential of undergoing vinyl addition copolymerization, and subsequently reacting with suitable cross-linking agents to form a cross-linked polymer by thermal treatment. The determination of reactivity ratios of monomer pairs in copolymerization reactions is of considerable importance, since the chemical composition of a copolymer depends mainly upon the relative reactivities of the two monomers toward the two intermediate radicals. Studies of the relative reactivities of vinyl monomers have been numerous, but similar information on conjugated diene monomers is less extensive. The purpose of this investigation was to homopolymerize 1 and 2, and to copolymerize them with each other as well as with styrene, so that some comparison of their relative reactivity in free-radical-initiated polymerizations could be made.



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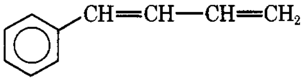

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Results and Discussion

Homopolymerization. The free-radical homopolymerization of 1 in degassed benzene solution at 70° with azodiisobutyronitrile as an initiator provided poly(butadienylferrocene) in 37% conversion (Figure 1). The polymer was a brown powder with a softening point of 140° and $\bar{M}_n$ of 1650 (VPO). This is in contrast to a recent preliminary study[2] of the polymerization characteristics of 1,

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[1] E. W. Neuse and H. Rosenberg, *J. Macromol Sci.-Rev. Macromol. Chem.*, 4, 1 (1970).

[2] D. C. Van Landuyt and S. F. Reed, Jr., *J. Polym. Sci., Part A-1*, 9, 523 (1971).

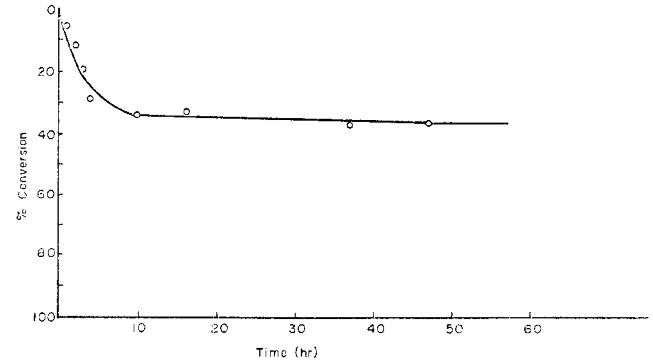


Figure 1. Homopolymerization of 1-ferrocenyl-1,3-butadiene at 70°.

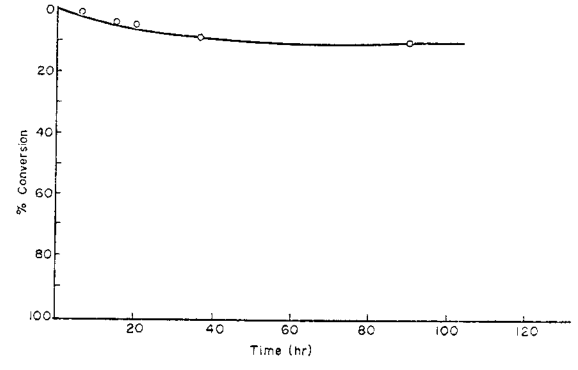


Figure 2. Homopolymerization of 1-phenyl-1,3-butadiene at 70°.

which revealed only a low yield of dimeric product obtained only at high initiator concentrations. We have determined the rate of homopolymerization of this monomer by following its disappearance by means of glpc and by nmr. Table I gives the data for these homopolymerizations obtained at 70°. The rate constant ($k = R_p/[M][I]^{1/2}$) is 1.50×10^{-4}, which is very close to those reported[3] for vinylferrocene and styrene at 70° ($k_{VF} = 1.8 \times 10^{-4}$; $k_{Sty} = 1.65 \times 10^{-4}$).

The free-radical-induced homopolymerization of **2** was carried out to 11% conversion (Figure 2) by the same method as outlined above. The homopolymer was a white solid with $\bar{M}_n$ of 1100 (VPO). The rate was determined by monitoring the disappearance of **2** by glpc. The rate constant (Table I) is 7.4×10^{-6}.

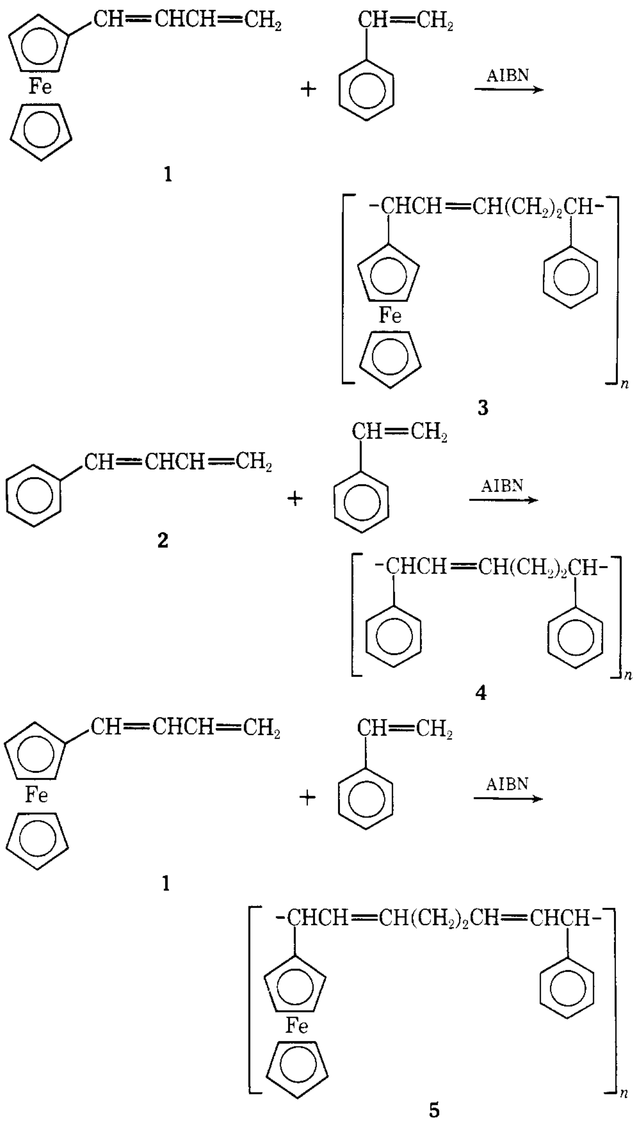
Copolymerizations. Since one would expect monomers **1** and **2** to have copolymerization characteristics somewhat similar to styrene, and since extensive copolymerization data are already available on styrene,[4] solution copolymerization reactions between these monomers and styrene were studied. These copolymerization reactions were carried out in a benzene solvent within evacuated sealed polymerization vessels at 70°. The progress of the polymerization was monitored variously by dilatometry, glpc, and nmr. Gas-liquid partition chromatography was found to be particularly useful in this regard, since very accurate per cent conversion *vs.* time data could easily be obtained by this method. The polymerization reactions were stopped at relatively low percentage conversion so that a major change in monomer concentration from the initial charge did not occur, and consequently, the general method for the solution of the copolymer equation could be used.

Table I
Homopolymerization of 1-Ferrocenyl-1,3-butadiene and 1-Phenyl-1,3-butadiene at 70°

Monomer	[M]	[AIBN]	$R_p/[M][I]^{1/2}$	$\bar{M}_n$ (VPO)
1-Ferrocenyl-1,-3-butadiene	0.045	0.007	1.50×10^{-4}	1650
1-Phenyl-1,-3-butadiene	0.714	0.012	7.4×10^{-6}	1100

The copolymerization of monomers **1** and **2** with styrene and with each other produced the copolymers **3**, **4**, and **5** (Scheme I). The polymers were isolated by precipitation into methanol and purified several times by recipitation, and then dried.

Scheme I



A mixture of cis and trans stereoisomers was used for all polymerizations of the two substituted butadiene monomers. The trans isomer of both 1-phenyl-1,3-butadiene and 1-ferrocenyl-1,3-butadiene was found to undergo polymerization to a greater per cent conversion than the cis isomer. These isomers are easily separated by glpc when proper conditions are employed. Monomer **1** exhibits a uv

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(3) M. G. Baldwin and K. E. Johnson, *J. Polym. Sci., Part A-1*, 5, 2091 (1967).

(4) H. Mark, B. Immergut, E. Immergut, L. Young, and K. Beyon in "Copolymerization," G. E. Hamm, Ed., Interscience-Wiley, New York, N. Y., 1964, Appendicies A and B.

Table II
Reactivity Ratios for Copolymerization of Styrene (M_1) with Comonomer (M_2)

	Linearization Procedure		Integrated Form	
Comonomer (M_2)	r_1	r_2	r_1	r_2
1-Ferrocenyl-1,3-butadiene	0.76 ± 0.01	2.47 ± 0.01	0.67 ± 0.10	2.26 ± 0.20
1-Phenyl-1,3-butadiene	0.71 ± 0.01	1.20 ± 0.0	0.72 ± 0.02	1.06 ± 0.01

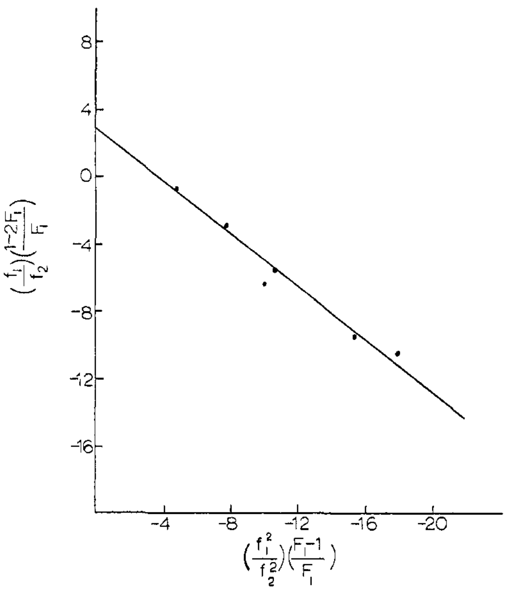

Figure 3. Fineman-Ross plot for copolymerization of styrene (M_1) and 1-ferrocenyl-1,3-butadiene (M_2).

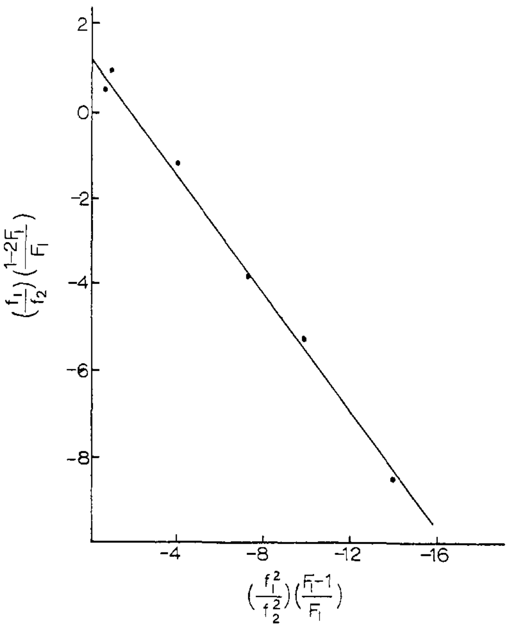

Figure 4. Fineman-Ross plot for copolymerization of styrene (M_1) and 1-phenyl-1,3-butadiene (M_2).

maximum in ethanol at 243 nm (cis) and at 285 nm for the trans isomer. Monomer **2** was found to give maxima at 266 nm (cis) and at 279 nm (trans) which correspond to the reported values for 1-phenyl-1,3-butadiene.[5]

The glpc data obtained for the copolymers has been used to calculate the reactivity ratios for the different monomer pairs by the direct use of the copolymer equation and by the use of the integrated form of this equation. The first method involves the Fineman and Ross linearization method (eq 1).[6] When the term on the left-hand

$$\left(\frac{f_1}{f_2}\right)\left(\frac{1-2F_1}{F_1}\right) = \left[\left(\frac{f_1^2}{f_2^2}\right)\left(\frac{F_1-1}{F_1}\right)\right]r_1 + r_2 \qquad (1)$$

side of eq 1 is plotted *vs.* the coefficient of r_1, a straight line is obtained whose slope is r_1 and whose intercept is r_2. Figure 3 shows a typical plot for copolymerization of styrene and 1-ferrocenyl-1,3-butadiene and Figure 4 shows the corresponding plot for styrene and 1-phenyl-1,3-butadiene. A computerized version[7] of the Fineman and Ross linearization procedure was also used to calculate the reactivity ratios from eq 2 and 3. In these equations, G is

$$F/G(G-1) = r_1(F^2/G) - r_2 \qquad (2)$$

$$(G-1)/F = -r_2(G/F^2) + r_1 \qquad (3)$$

the ratio of monomer M_1 to monomer M_2 in the initial reaction mixture and $F = m_1/m_2$, where m_1 and m_2 are the concentrations of the monomer units incorporated into the polymer.

The second method involves the integrated form of the copolymerization equation[8] (eq 4). Again, utilization of a

$$r_2 = \frac{\log(M_2^0/M_2) - (1/P)\log(1-p)(M_1/M_2)/(1-P)(M_1^0/M_2^0)}{\log(M_1^0/M_1) + \log(1-P)(M_1/M_2)/1-P(M_1^0/M_2^0)}$$

$$P = (1-r_1)/(1-r_2)$$

computerized version[9] of this technique allowed the determination of the reactivity ratios. Table II gives a comparison of the r_1 and r_2 values obtained by the two different methods for the copolymerizations studied. The two methods gave values which are in fairly close agreement, although the values for monomer **2** show slightly more consistency than those for monomer **1**. It is significant that while r_2 for butadienylferrocene is larger than r_2 for butadienylbenzene, both of these values are greater than one.

The Q and e values for both monomers **1** and **2** were determined, and are listed in Table III. As might be expected, these values are in the same range as those of styrene (Q = 1.0; e = −0.8).[10] The e values determined for monomers 1 and 2 from data obtained in their copolymerization reactions with styrene agree quite well with each other

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(5) O. Grummitt and F. G. Christoph, *J. Amer. Chem. Soc.*, **73**, 3479 (1951).

(6) M. Fineman and S. D. Ross, *J. Polym. Sci.*, **5**, 259 (1950).

(7) S. P. Chang, T. K. Miwa, and W. H. Tallent, *J. Polym. Sci., Part A-1*, **7**, 471 (1969).

(8) F. R. Mayo and F. M. Lewis, *J. Amer. Chem. Soc.*, **66**, 1594 (1944).

(9) D. R. Montgomery and C. E. Fry, *J. Polym. Sci., Part C*, **25**, 59 (1968).

(10) G. E. Ham, "Copolymerization," Interscience, New York, N. Y., 1964, p 861.

Table III
Q and e Values for Monomers 1 and 2

Monomer	Q	e
1-Ferrocenyl-1,3-butadiene (**1**)	1.56	−0.80
1-Phenyl-1,3-butadiene (**2**)	1.49	−0.79

Table IV
Solution Copolymerization of 1-Ferrocenyl-1,3-butadiene and Styrene at 70°

No.	Mole Ratio Styrene in Feed	Mole Ratio Styrene in Copolymer	Time (hr)	% Conversion Styrene	$\bar{M}_n$ Copolymer
1	11.02	8.05	21	11.70	1950
2	7.75	5.88	20	5.70	1775
3	8.10	6.45	20	4.50	1725
4	6.67	5.00	21	12.48	1650
5	4.87	2.41	21	13.05	1530
6	2.55	1.41	21	3.82	1300

and with the −0.8 of styrene. The Q values agree quite well for the two monomers **1** and **2**, but there is a significant difference between these values and the value of 1.0 for styrene. One would expect a larger resonance contribution to the stability of the intermediate radicals from monomers **1** and **2** than from styrene, and thus, the observed difference in Q values for these systems is not surprising.

Copolymerization reactions were also carried out between 1-ferrocenyl-1,3-butadiene and 1-phenyl-1,3-butadiene. In this case, however, no suitable reactivity ratios could be obtained, due to the extremely low molecular weight of the polymer product. Even though the percentage conversion of these monomers in this copolymerization attempt was about the same as in their copolymerization with styrene, the product seemed to be mostly dimeric material ($\bar{M}_n$ = 570). This failure to form a copolymer of higher molecular weight in this case is probably due to a combination of steric factors between monomers **1** and **2**, and to the high chain transfer reactivity of these allylic radicals.

Experimental Section

Preparation of Starting Materials. 1-Phenyl-1,3-butadiene was prepared by the method of Grummitt and Christoph[5] and was purified by distillation. 1-Ferrocenyl-1,3-butadiene was prepared by the method of Ponder *et al.*[11] Reagent grade styrene was washed with 5% KOH, dried, and distilled under reduced pressure, with a center cut being used for all polymerizations. AIBN initiator was recrystallized from methanol, mp 102–105.[6] Benzene solvent was distilled from calcium hydride.

Table V
Solution Copolymerization of 1-Phenyl-1,3-butadiene and Styrene at 70°

No.	Mole Ratio Styrene in Feed	Mole Ratio Styrene in Copolymer	Time (hr)	% Conversion	$\bar{M}_n$ Copolymer
1	9.80	7.17	21	3.6	2880
2	6.67	4.55	21	2.2	3800
3	4.87	3.82	21	3.2	2700
4	2.59	1.72	21	2.1	3100
5	0.61	0.595	21	9.8	2200
6	0.33	0.243	21	2.0	1700

Apparatus and Equipment. For the glpc analyses, a Varian series 1520 dual-column chromatograph was employed. Concentration measurements were made with the aid of a disc integrator, using the internal standard technique. For the glpc analysis of the copolymerization of monomer **1** with styrene a 5 ft × ⅛ in. ss column packed with 5% SE-30 on Chromosorb G was used. The copolymerization analysis of monomer **2** with styrene required a 6 ft × ¼ in. column packed with 15% Carbowax 20M on Chromosorb P. The copolymerization of monomer **1** with monomer **2** was followed using the dilatometric method of Baldwin.[12] Number-average molecular weights were determined in chloroform solution by the isopiestic method utilizing a Hitachi Perkin-Elmer Model 115 osmometer, which had previously been calibrated utilizing commercially available polystyrene standards.

Free-Radical Copolymerization. The free-radical copolymerizations of styrene with monomers **1** and **2** were all carried out in a similar manner. A typical polymerization which yielded polymer 4 (Table IV) was run as follows: a mixture of styrene, 1-phenyl-1,3-butadiene, AIBN initiator, internal standard (toluene), and solvent (benzene) was placed in a two-necked flask fitted with a septum and stopcock. The contents of the flask was degassed by several freeze–thaw cycles using liquid nitrogen, and the system was then placed under a slight positive pressure of oxygen-free nitrogen. Before polymerization was started, a sample of the reaction solution was withdrawn by means of a hypodermic syringe and analyzed by glpc. The reaction flask was then immersed in a constant-temperature bath at 70° and maintained at this temperature for 21 hr. At this time, a final sample was made and analyzed on the glpc instrument. The contents of the polymerization flash were then poured into 200 ml of methanol, and the precipitated white polymer was filtered, reprecipitated, and then dried.

A summary of monomer concentrations, per cent conversions, and polymer compositions is given in Tables IV and V.

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(11) B. W. Ponder, R. Craig Kneisel, and Danny H. Lewis, *Org. Prep. Proc. Intr.*, 3(4), 171 (1971).

(12) M. G. Baldwin, *J. Polym. Sci., Part A*, **1**, 3209 (1963).