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Hammett Relations in Anionic Polymerization. Reaction of Polystyrylalkali Salts with Disubstituted 1,1-Diphenylethylenes

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ABSTRACT: In order to obtain a better understanding of the role of the cation and of the carbanionic part of the active center in the growth step of anionic polymerizations in nonpolar media, the Hammett relation was examined for the reaction of various disubstituted 1,1-diphenylethylenes with the Li^+, K^+, and Cs^+ salts of living polystyrene in benzene at 24 °C, diphenylethylenes being chosen as monomers because they do not further polymerize after one addition step and allow a simple spectrophotometric determination of the rates. The Hammett plots all yielded positive ρ values, increasing from ca. +1.8 for the Li^+ salt to +2.2 for the K^+ salt and +2.4 for the Cs^+ salt. These values, which all pertain to the reaction of ion pairs containing different cations, are to be compared with the ρ value of +2.8 to +3.5 obtained for the same type of reaction with the K^+ salt of living polystyrene in THF, where ρ may be assumed to be largely determined by the reaction of free carbanions. The results combined with some known data from the literature suggest that in the absence of stronger coordinating molecules, such as ethereal solvents, complexation of the monomer with the positive counterion or participation of this ion in polarizing the double bond of the monomer constitutes a characteristic feature of the propagation reaction of anionic polymerization in the presence of alkali salts, at least with lithium as a counterion. In order to check a possible influence of the π electrons of benzene, the addition of the different disubstituted diphenylethylenes to the Li^+ salt of living polystyrene was also studied in cyclohexane, allowing a direct comparison with the results obtained for this salt in benzene.

During the last decade, much attention has been paid in mechanistic studies of anionic polymerizations to solvent effects or to complexation of the active species with different donor agents. However, in spite of the vast amount of results, the detailed mechanism of the main step of the polymerization process (the propagation reaction) is still not clear, particularly for polymerizations of vinyl monomers in nonpolar solvents with alkali metals as counterions.

The question arises as to whether the C=C bond of the monomer could participate in the coordination with the positive counterion, prior to its addition to the polymeric chain end, if other coordinating agents, like ethers, are absent. Although no direct proof was provided for complex formation with the monomer during anionic chain propagation, some spectroscopic evidence was found for monomer–counterion type complexes in compounds such as 3-butenyl-[1] or 5-methyl-2-heptenyllithium.[2] Two types of anionic polymerizations are contemplated:[3–6] the direct one-step propagation and the two-step reaction in which the monomer is first associated with a cation yielding an intermediate complex, whereafter the spontaneous rearrangement of the latter produces the original living polymer but by one unit longer.

The latter mechanism was discussed by Medvedev[5] and seems to be plausible in anionic polymerizations proceeding in nonpolar media with lithium as counterion. Formation of such a complex may account for the stereospecificity of diene polymerization induced by organolithium compounds in nonpolar media. In fact, substitution of Li^+ by Na^+ and K^+ decreases the 1,4-cis content.[5,7]

Two observations support the hypothesis that the coordination of monomer with cation is operative in chain growth. The second order with respect to the monomer concentration, as observed in studies of polymerization of isoprene,[8] was accounted for by assuming chain growth involving an activated monomer formed by an association of isoprene with a monomeric growing chain end.

Similarly, in the reaction of butyllithium (BuLi) with a large excess of styrene in benzene, π-complex formation between the Li^+ cation and styrene, which would break up the hexameric aggregates of BuLi into trimers, was suggested to explain the observed one-third order with respect to the BuLi concentration, instead of the usual one-sixth order in this nonpolar solvent.[9] The slowing down of the reaction rate by carrying out the polymerization in the presence of durene, being a better complexing agent than the monomer, seemed to support this assumption.[10]

The problem of monomer complexation resulting in a two-stage propagation reaction leads to the interesting question which stage is the rate-determining step in such systems? Further information about this may be obtained from Hammett relation studies. Indeed work by Natta et al.[11] indicated a negative ρ value ($\rho = -0.95$) for the anionic co-

Table I

	DP_{calcd}[a]	λ_{max}, nm	ϵ	$Concn_{calcd}$, M	Ref
PSt^-Li^+ in benzene	260	334	1.30×10^4	1×10^{-3}	22
PSt^-Li^+ in cyclohexane	150	328	1.35×10^4	5×10^{-3}	25
PSt^-K^+ in benzene[b]	175	329	1.30×10^4	1×10^{-3}	24
PSt^-K^+ in THF[b]	150	343	1.20×10^4	5×10^{-4}	15
PSt^-Cs^+ in benzene[b]	250	333	1.30×10^4	4×10^{-4}	24

[a] The degree of polymerization was calculated from the monomer to initiator ratio. [b] Two-ended living polymers.

polymerization of various substituted styrenes with living polystyrene initiated by coordination catalysts. The negative value implies that the active center in this anionic polymerization behaves as an electrophile, i.e., the coordination of the monomer with the electropositive transition metal of the catalyst appears to be the rate-determining step. It should be mentioned that two Hammett relation studies leading to positive ρ values were reported in the literature. Thus a ρ value of +1 was found for the initiation reaction of substituted styrenes with n-BuLi in benzene(12) ($\rho = +1$), and a ρ value of +5 was found for the copolymerization of polystyrylsodium with a series of substituted styrenes in tetrahydrofuran (THF).[13] In the case of the polymerization in THF, the rate of propagation of living polystyrylsodium is largely determined by a small fraction of very reactive free carbanions being in rapid equilibrium with the solvated ion pairs,[14,15] and as a consequence we are dealing in this case with an example of a one-step mechanism. In the systems in which both species contribute the ρ values should be computed separately for free ions and ion pairs. This was done by Ise et al.[16] Unfortunately, in this report only homopolymerization of substituted styrenes was studied, and as a consequence, reactivities not only of the monomers but also of the living ends are reflected in their results. The nonassociated and unsolvated ion pairs are considered as the only active species for the propagation reaction in nonpolar media and the carbanionic or the cationic part of the active center or both may be involved in the growth step. In order to elucidate the role of the cation, it seemed therefore particularly interesting to examine the Hammett relation in these systems and for this purpose alkali salts of living polystyrene were reacted in different solvents with substituted 1,1-diphenylethylenes, these monomers being chosen for two reasons. First, since 1,1-diphenylethylene does not polymerize further after one addition to the living polystyrene due to steric hindrance,[17] the interpretation of the results is greatly simplified in comparison with studies of homopolymerization of substituted styrenes where the substituent may affect the reactivity of both monomer and active center,[16] or where special experimental conditions and techniques are required to isolate the first addition step.[13] Second, the reaction can easily be followed spectrophotometrically, as the absorption maximum of living polystyrene (ca. 335 nm) and of the resulting adduct, viz., living 2-polystyryl-1,1-diphenylethylene (ca. 440 nm) are sufficiently separated to permit accurate measurement of the changes in optical density.

Experimental Section

All the experiments were carried out under high vacuum in all-glass sealed apparatus. Commercial solvents (benzene, cyclohexane, and THF) of high purity grade were degassed, dried over Na K alloy and stored over the alloy on the vacuum line. Before use, the nonpolar solvents were distilled into a smaller reservoir containing butyllithium from which the solvent had been removed and from there transferred to the reaction vessel by distillation.

Purified styrene and α-methylstyrene were dried twice with calcium hydride under high vacuum and then distilled in an apparatus containing Na K alloy and sealed off from the vacuum line. Part of the monomer was then brought in contact with the alloy and after reaction transferred again to the bulk, this drying operation being repeated until the characteristic color of the resulting dianions persisted. Finally, the monomer was distilled into ampules, sealed off, and stored at −10 °C.

The following 1,1-diphenylethylenes were investigated: 1,1-diphenylethylene (DPE), bp 123–125 °C (5 mm); p,p'-$(Me)_2$-DPE, mp 61–62 °C; p,p'-$(t\text{-}Bu)_2$-DPE, mp 89.5–90.5 °C; p,p'-$(MeO)_2$-DPE, mp 143 °C; p,p'-F_2-DPE, mp 24 °C, bp 73 °C (0.5 mm); p,p'-$(CF_3)_2$-DPE, mp 34–35 °C; m,m'-$(Me)_2$-DPE, bp 120 °C (1 mm); m,m'-$(MeO)_2$-DPE, bp 161 °C (2 mm); and m,m'-Cl_2-DPE, bp 145 °C (1.5 mm). They were prepared by Grignard reaction from ethyl acetate and the respective substituted phenylmagnesium bromides, following the procedure described for the unsubstituted compound.[18] The meta-substituted monomers were purified by fractional distillation on a spinning band column, and the para-substituted derivatives, being obtained in crystalline state, were purified by repeated recrystallization from methanol or methanol–benzene and dried under high vacuum. All the monomers, the purity of which was checked by gas chromatography and found satisfactory, were diluted under vacuum with the appropriate solvent to a known concentration and stored in ampules in the refrigerator.

Special care was taken in the purification of the alkyllithium initiators used, since it has been shown that impurities and especially alcoholates may substantially influence the kinetics in anionic polymerization.[19,20] Ethyllithium (Fluka, suspension in benzene) was recrystallized several times under high vacuum until a colorless solution was obtained, and *sec*-butyllithium (Metallgesellschaft, solution in isopentane) was purified by a short-path distillation under vacuum using an apparatus equipped with a cold finger. Dilutions were achieved under high vacuum and concentrations of the organolithium compound and the amount of residual alcoholates present (less than 1%) were determined by the double titration method of Gilman.[21]

Living polystyryllithium in benzene was produced by initiating the polymerization of styrene with ethyllithium. To avoid interference in the rate measurements by the presence of unreacted initiator in the living polymer solution, the ratio of monomer to initiator was such that the initiation was completed rapidly compared with the propagation reaction.[22] Since the initiation in nonaromatic solvents was accompanied by an induction period,[23] the more reactive *sec*-butyllithium was used as initiator for the preparation of polystyryllithium in cyclohexane, with about the same degree of polymerization as in benzene. The potassium salt of living polystyrene in benzene and in THF was formed by contacting α-methylstyrene with a film of the alkali metal, as described by Roovers et al.,[24a] and the resulting active oligomer was then used to initiate the polymerization of styrene. Similarly, polystyrylcesium in benzene was obtained by reacting for a short time a 1% styrene solution in benzene with a film of cesium (Schuchardt, 99.9%).

In this way, stock solutions of living polystyrene polymers were prepared, divided into ampules, and stored in the refrigerator for 2 weeks at most. For each preparation, the initiation reaction was followed spectrophotometrically at the absorption maximum of the polystyryl anion, and the concentration of living ends was determined using the extinction coefficients reported in the literature, the pertinent data being listed in Table I.

Solutions of polystyrylpotassium in THF as well as in benzene were unstable. The absorption band at 330 nm slowly decreased in intensity and a new band at about 530 nm appeared, as was also observed before.[24a,26] Not only the living end concentration was affected by this isomerization reaction but also the kinetics of the addition of 1,1-diphenylethylene were modified, the rate being several times higher for the reaction with freshly prepared polystyrylpotassium, and therefore rate measurements were always made as rapidly as possible after forming the living polymer solution.

Rates of addition of 1,1-diphenylethylenes to the living polymers were determined spectrophotometrically with a Cary 17 instrument at 24 °C, using an apparatus similar to that depicted on p 185 of ref 7. Before each kinetic run, the complete unit was rinsed under vacuum with a concentrated solution of the polystyrylalkali salt under in-

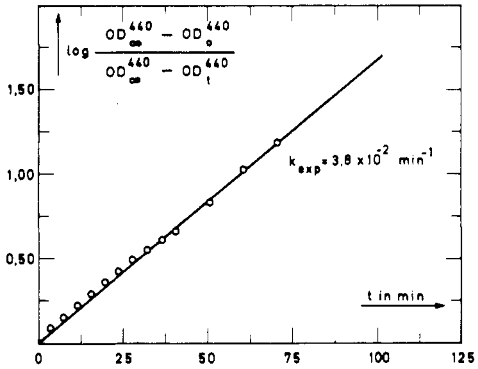

Figure 1. First-order plot for the reaction of PSt^-Li^+ with 1,1-diphenylethylene in benzene (T = 24 °C, $[PSt^-Li^+] = 9 \times 10^{-4}$ M, $[DPE]_0 = 5 \times 10^{-5}$M).

Table II
Reaction of PSt^-Li^+ with Substituted 1,1-Diphenylethylenes in Benzene (T = 24 °C; $[DPE]_0 = 5 \times 10^{-5}$ M)

Substituent	$[PSt^-Li^+]_{tot} \times 10^4$,[a] M	$k_{exptl} = k_p'[PSt^-Li^+]_{tot}^{1/2} \times 10^2$, min^{-1}	k_p', $M^{-1/2}$ min^{-1}
H	9.0	3.8	1.27
	8.6	3.85	1.31
m,m'-(MeO)$_2$-	9.5	9.0	2.90
m,m'-(Me)$_2$-	9.3	3.5	1.15
	13.0	4.0	1.11
p,p'-(Me)$_2$-	9.6	1.1	0.35
	8.1	1.0	0.35
p,p'-(MeO)$_2$-	12.7	0.22	0.06

[a] Determined using the extinction coefficient 13 000.[22]

Table III
Reaction of PSt^-Li^+ with Substituted 1,1-Diphenylethylenes in Cyclohexane (T = 24 °C; $[DPE]_0 = 3 \times 10^{-4}$ M)

Substituent	$[PSt^-Li^+]_{tot} \times 10^3$, M	$k_{exptl} = k_p'[PSt^-Li^+]_{tot}^{1/2} \times 10^2$, min^{-1}	k_p', $M^{-1/2}$ min^{-1}
H	4.85	4.8	0.69
m,m'-(MeO)$_2$-	4.3	14.0	2.15
m,m'-(Me)$_2$-	5.1	4.5	0.62
p,p'-(Me)$_2$-	5.1	0.95	0.14
p,p'-(*t*-Bu)$_2$-	4.3	1.94	0.29
p,p'-(MeO)$_2$	4.3	0.23	0.03

vestigation to destroy all impurities and residual moisture. The solution was then returned to an attached reservoir, which was sealed off after the walls of the apparatus were thoroughly washed with solvent distilled from this wash solution. For the rate measurement, the optical cell was not sealed off from the apparatus but was directly immersed in a quartz Dewar with optical windows placed in the cell compartment of the spectrophotometer and containing thermostatized methanol to maintain the total volume of the reaction mixture at constant temperature, so that inner distillation of solvent with concomitant concentration changes in the optical cell during the measurement was prevented.

Results

Polystyryllithium. Living polystyryllithium (PSt^-Li^+) exists in nonpolar solvents such as benzene and cyclohexane largely in the form of unreactive dimeric aggregates and the propagation of the polymerization proceeds via a low concentration of unassociated ion pairs, being in equilibrium with the dimers.[22] The rate expression for the addition of 1,1-diphenylethylene (DPE) is thus given by:

$$-\frac{d[DPE]}{dt} = k_p'[PSt^-Li^+]_{tot}^{1/2}[DPE]$$

where k_p' equals $k_pK_d^{1/2}/2^{1/2}$, k_p being the intrinsic propagation rate constant for the ion pairs and K_d the equilibrium constant for the dissociation of the dimers. Indeed experiments performed in the presence of an excess of PSt^-Li^+ showed the reaction to be first order in DPE, the pseudo-first-order rate constant, k_{exptl}, being proportional to the total concentration of PSt^-Li^+. The data were obtained spectrophotometrically by observing the conversion of living polystyryllithium into 2-polystyryl-1,1-diphenylethyllithium ion ($PDPE^-Li^+$) absorbing at 440 nm. In fact, since DPE adds only once to the polystyryl moiety, the initial 1,1-diphenylethylene concentration $[DPE]_0$ equals the concentration of $PDPE^-Li^+$ at the end of the reaction $[PDPE^-Li^+]_\infty$, and the variable 1,1-diphenylethylene concentration $[DPE]_t$ is then given by $[PDPE^-Li^+]_\infty - [PDPE^-Li^+]_t$. Accordingly, the progress of the reaction is followed by monitoring the increase of the optical density at the absorption maximum of the newly formed ion pair (ca. 440 nm). This leads then to the following form for the rate expression:

$$\log \frac{OD_\infty^{440} - OD_0^{440}}{OD_\infty^{440} - OD_t^{440}} = \frac{k_{exptl}}{2.3} t$$

OD_∞^{440}, OD_0^{440}, and OD_t^{440} being respectively the optical density measured at 440 nm at the end of the reaction, at time zero, and at time t.

In each run, the plot of this logarithmic function vs. time was linear, as exemplified by the graph shown in Figure 1, and the slopes of the lines multiplied by the factor 2.3 yielded the pseudo-first-order rate constants, denoted by k_{exptl}. The rate expression also shows that the value of the extinction coefficient for the different $PDPE^-Li^+$ species need not be known using this technique.

The results of the rate measurements in benzene and in cyclohexane are presented in Tables II and III, and from the agreement between the values of k_p' for some duplicated experiments, it may be concluded that the techniques used were sufficiently rigorous to obtain reproducible results.

An attempt was made to investigate the rate of addition of *p,p'*-F_2-DPE, *m,m'*-Cl_2-DPE, and *p,p'*-$(CF_3)_2$-DPE to polystyryllithium. Unfortunately the resulting ions are unstable and the side reactions prevented us from determining accurately the rates of addition.

In the course of this work we also determined the absorption maximum at which the reaction was followed as well as the extinction coefficients by converting quantitatively polystyryllithium in benzene into the respective substituted 2-polystyryl-1,1-diphenylethyllithium compounds and by neutralizing part of the living ends with a known amount of *tert*-butyl alcohol. The relevant data are collected in Table IV.

Polystyrylpotassium and Polystyrylcesium in Benzene. The above studies were extended to the addition of a series of 1,1-diphenylethylenes to polystyrylpotassium and polystyrylcesium. The same spectrophotometric technique was used throughout this study, the rates being monitored at 475 nm for potassium and at 480 nm for cesium. The results are given in Tables V and VI. The pseudo-first-order rate constants k_{exptl} are again composite values, dependent on the constant concentration of the active PSt^-M^+ ends. However,

Table IV
Absorption Maxima and Extinction Coefficients for Different Substituted 2-Polystyryl-1,1-diphenylethyllithium Compounds in Benzene

Substituent	λ_{max}, nm	ϵ_{max}
H	440	15 700
m,m'-(Me)$_2$-	423	17 650
p,p'-(Me)$_2$-	423	20 900
m,m'-(MeO)$_2$-	440	12 700
p,p'-(MeO)$_2$-	435	14 200
p,p'-(t-Bu)$_2^-$	430	20 400
Polystyryllithium	334	13 000[22]

Table V
Reaction of PSt^-K^+ with Substituted 1,1-Diphenylethylenes in Benzene (T = 24 °C; $[DPE]_0 = 4 \times 10^{-5}$ M)

Substituent	$[PSt^-K^+]_{tot} \times 10^4$, M	$[PSt^-K^+]_{calcd} \times 10^4$,[a] M	$k_{exptl} = k_p \times [PSt^-K^+]_{calcd} \times 10^3$, s^{-1}	k_p, M^{-1} s^{-1}
H	8.6	4.1	40	98.0
	9.1	4.2	46.6	109.8
m,m'-(MeO)$_2$-	9.2	4.2	68.3	160.8
m,m'-(Me)$_2$-	8.6	4.1	18.8	45.9
	9.15	4.2	21.1	49.8
p,p'-(Me)$_2$-	8.6	4.1	6.5	15.8
	9.2	4.2	8.6	20.2
p,p'-(t-Bu)$_2$-	8.6	4.1	4.7	11.4
	9.2	4.2	5.8	13.7
p,p'-(MeO)$_2$-	8.85	4.1	1.3	3.2

[a] Concentration of free ion pairs.

Table VI
Reaction of PSt^-Cs^+ with Substituted 1,1-Diphenylethylenes in Benzene (T = 24 °C)

Substituent	$[PSt^-Cs^+]_{tot} \times 10^4$, M	$[DPE]_0 \times 10^5$, M	$k_{exptl} = k_p[PSt^-Cs^+]_{tot} \times 10^3$, s^{-1}	k_p, M^{-1} s^{-1}
H	3.45	3.0	20.6	60.0
	2.7	2.8	14.3	53.4
m,m'-(MeO)$_2$-	3.4	3.0	39.0	114.7
m,m'-(Me)$_2$-	3.7	3.0	9.0	24.3
	2.7	2.8	6.0	22.2
p,p'-(Me)$_2$-	3.7	3.0	3.3	9.1
	2.7	2.8	2.1	8.0
p,p'-(t-Bu)$_2$-	4.85	4.5	3.6	7.5
p,p'-(MeO)$_2$-	5.0	4.0	0.75	1.5
	1.0	300	4.7 (k_p[DPE])	1.6[a]

[a] Value obtained for the reaction carried out with an excess of olefin by plotting log $(OD_0^{330} - OD_\infty^{330})/(OD_t^{330} - OD_\infty^{330})$ vs. time and after making a correction for about 10% of living chain end termination. See Appendix.

Table VII
Reaction of PSt^-K^+ with Substituted 1,1-Diphenylethylenes in THF (T = 24 °C; $[DPE]_0 = 6 \times 10^{-5}$ M)

Substituent	$[PSt^-K^+]_{tot} \times 10^4$, M	$k_{exptl} = k_p[PSt^-K^+]_{tot}$, s^{-1}	k_p, M^{-1} s^{-1}
H	4.7	>1[a]	>2130 5000[b]
m,m'-(Me)$_2$-	4.7	0.35	745
p,p'-(Me)$_2$-	4.7	0.16	340
p,p'-(t-Bu)$_2$-	4.7	0.145	310
p,p'-(MeO)$_2$-	4.7	0.025	53

[a] The increase in optical density at 475 nm is too rapid to be measured accurately. [b] Calculated from $k_p = k_\pm + k_- K_d^{1/2}[PSt^-K^+]_0^{-1/2}$ with $K_d = 0.7 \times 10^{-7}$ M[15] and $k_- = 400\,000$ M^{-1} s^{-1} by analogy with the value of k_- for the reaction PSt^-Na^+ + DPE (THF; 25 °C).[29]

association to dimers for these polysytrylalkali salts in benzene is less pronounced than for polystyryllithium.[24a] In the concentration range studied here, the polystyrylcesium ion pairs are not associated,[24a] and the absolute reaction constant for the ion pair k_p was obtained therefore simply by dividing k_{exptl} by the total concentration of active ends, as determined from the absorption spectrum at 333 nm using the extinction coefficient already mentioned above (Table I).

On the other hand, polystyrylpotassium shows an intermediate behavior, being associated to dimers only at concentrations higher than 10^{-3} M, and existing as free ion pairs at concentrations of about 5×10^{-5} M.[24a] Consequently, at intermediate concentrations, where appreciable amounts of dimer and monomer are present, the rate constant is given by a complicated function of the dissociation constant and of the total concentration of active ends,

$$k_p' = \{-K_d/2 + [(K_d/2)^2 + 4(K_d/2)[PSt^-K^+]]^{1/2}\}k_p/2$$

so that for the determination of the absolute rate constant for the ion pair k_p, the equilibrium concentration of the reactive unassociated ion pairs has to be calculated. This was accomplished, given the spectrophotometrically determined total concentration of living polystyrylpotassium ends and the dissociation constant of the ion pair dimer K_d at 24 °C. From the known value of K_d at 20.3 °C and from the heat of dissociation ΔH_d, it was calculated that for polystyrylpotassium in benzene $K_d = 7.3 \times 10^{-4}$ M at 24 °C.

Polystyrylpotassium in THF. In order to compare the reactivity of free carbanions with that of ion pairs in benzene, the rate constants for addition of a series of substituted 1,1-diphenylethylenes to an excess of polystyrylalkali salt were measured also in THF, using the same spectrophotometrical method as described above for the reactions in nonpolar solvents (Table VII). However, the maximum rate that could still be measured accurately with this method was limited to a half-lifetime of about 1 s, and for this reason, the potassium salt was chosen for the investigation in THF, since for this salt the free ion contribution to the total rate in THF is still the predominant one while the dissociation of the ion pairs into free ions and therefore also the reaction rate was shown to be smaller than for the lithium and the sodium salt, the dissociation and the rate decreasing along the series Li > Na > K > Cs.[15]

The reactions were followed at 475 nm, and the apparent bimolecular rate constant k_p was obtained by dividing the experimental pseudo-first-order rate constant k_{exptl} by the constant total concentration of living ends, which was calculated from the optical density at the absorption maximum of PSt^-K^+ (343 nm) using an extinction coefficient of 12000.[15] It has been shown in previous studies[15] that the apparent bimolecular rate constant k_p is a function of the free ion pair rate constant $k_\pm$, the free ion rate constant k_-, and the dissociation constant of the ion pairs into free ions K_d and may be expressed by the relation:

$$k_p = k_\pm + k_- K_d^{1/2}[PSt^-K^+]_0^{-1/2}$$

Hence, from the value of K_d (7×10^{-8} M) and from the fact that the free carbanions are about 1000 times more reactive than the ion pairs, it is calculated that k_p at PSt^-K^+ con-

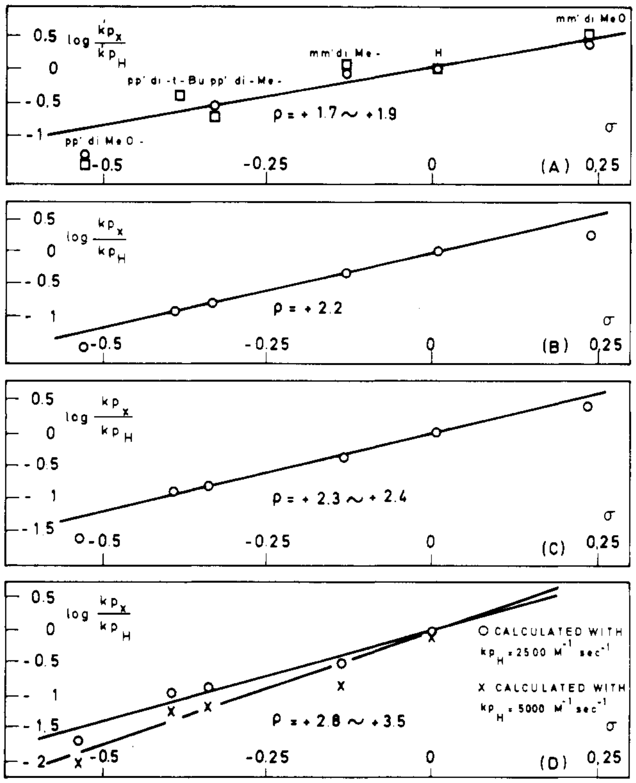

Figure 2. Hammett relations for the reaction of living polystyrenes (10^{-3} to 4×10^{-4} M) with disubstituted 1,1-diphenylethylenes ($\simeq 4 \times 10^{-5}$ M) at 24 °C: (A) PSt^-Li^+ in benzene (○) and in cyclohexane (□); (B) PSt^-K^+ in benzene; (C) PSt^-Cs^+ in benzene; (D) PSt^-K^+ in THF. For potassium and cesium salts in benzene, the relative absolute ion-pair rate constants k_{p_x}/k_{pH} were plotted against σ, whereas the relative composite constants k_{p_x}'/k_{pH}' were used for polystyryllithium. This does not matter however for the comparison of the respective values since the otherwise unknown value of K_d, which is included in k_p', cancels out as it is not influenced by the substituents on the various 1,1-diphenylethylene compounds.

centrations of 5×10^{-4} M is determined for about 90% by k_-, although only 1% of the ion pairs are dissociated into free ions at this concentration.

Hammett Relations. The relative rate constants for the addition reactions studied in the present work obey the Hammett relation, as shown by Figure 2. The experimental points fit fairly well straight lines; the ρ values were calculated using the least-squares method. The experimental difficulties in determining the rates for the reactions of PSt^-K^+ in THF, which are very fast, led to larger deviations of the calculated rate constants.

In the present study both phenyl groups in the 1,1-diphenylethylene molecule were equally substituted to preserve their equivalence, and in order to make the magnitude of the reactivity constant (ρ) comparable with other data in the literature, the substituent constants (σ) used here for the Hammett plots were taken to be twice the normal σ constants.[27]

The ρ values reflect the ratios of the rate constants of substituted to unsubstituted monomers irrespectively of whether the polystyryl salts are dimeric or monomeric. For the lithium salt, $\rho = +1.7$–1.9 is obtained, which is slightly lower than the value for the potassium and the cesium salt ($\rho \simeq +2.2$–2.4) in benzene. The addition reaction in THF gave a reactivity constant $\rho = +2.8$–3.5 for the apparent bimolecular rate constants k_p.

The ρ value in THF obtained in this work is substantially lower than the constant determined by Szwarc et al.[13] ($\rho = +5$) for the reaction of polystyrylsodium with substituted styrenes in THF. This might reflect the intrinsically higher reactivity of substituted 1,1-diphenylethylene monomers as compared with substituted styrenes.

Table VIII
Rate Constants for the Addition of Styrene and 1,1-Diphenylethylene to Living Polystyrene at 25 °C

	Styrene	Ref	1,1-DPE	Ref
PSt^-Li^+ (benzene) $2^{-1/2} k_pK_d^{1/2}$, $M^{-1/2}$ s^{-1}	0.9×10^{-2}	22	2.2×10^{-2} 2.1×10^{-2b}	*a* 30
PSt^-K^+ (benzene) k_p, M^{-1} s^{-1}	47	24	110	*a*
PSt^-Cs^+ (benzene) k_p, M^{-1} s^{-1}	18	24	60	*a*
PSt^-Li^+ (cyclohexane) $2^{-1/2} k_pK_d^{1/2}$, $M^{-1/2}$ s^{-1}	0.58×10^{-2}	28	1.2×10^{-2}	*a*
PSt^-Na^+ (THF) $k_{p\pm}$, M^{-1} s^{-1}	80	15	250	29

[a] This work, and at 24 °C. [b] The value 0.9×10^{-2} reported in ref 30 was found to be due to omission of the conversion factor 2.3. The experiment was repeated later confirming the value 2.1×10^{-2}.[31]

Discussion

One would anticipate that addition of 1,1-diphenylethylene to polystyrylalkali salts should be faster than that of styrene, due to an overall increase in resonance stabilization of the carbanionic species produced in the reaction with the former monomer. This is shown in Table VIII, where the rate constants for the addition of 1,1-diphenylethylene to different polystyryl salts and in different solvents are compared with the corresponding homopropagation rate constants, collected from literature. In all these systems, the addition of styrene is about 2.5 times slower than that of 1,1-diphenylethylene providing evidence for the accuracy of the results obtained in this work, since the other values are taken from different sources.

The Hammett plots for the different systems studied in the present work all yield straight lines passing through most of the points corresponding to reaction of 1,1-diphenylethylene and its substituted derivatives. Inspection of Figure 2 however reveals a significant deviation for the *m*- and *p*-methoxy-substituted olefins; these compounds were less reactive than expected from the linear relation. The respective points were therefore rejected in the least-squares calculation of the ρ values, except for the reaction in THF where the deviation is within the limits of experimental error. Such peculiar behavior of the methoxy derivatives was observed in a study of the Hammett relation for the initiation of a series of substituted styrenes with BuLi in benzene[12] and could arise from some side reaction, such as ring metallation of an aromatic nucleus of the diphenylethylene monomer at the ortho position of the methoxy substituent.[32,33] The formation of such charged species may lead to an inductive effect which will reduce the electrophilicity and therefore the reactivity of the metalled olefin even more then expected solely on the basis of the substituent effect of the methoxy group.

However, from kinetic considerations as well as from some additional experiments described in the Appendix, it was deduced that the metallation reaction is not the principal cause of the observed deviation.

Apparently the methox-substituted olefins are complexed with the cation and the net result of this complexation is a reduction of the reactivity. The fact that the deviation is less pronounced for the reaction in THF compared to the addition in benzene is further evidence in favor of this hypothesis. Finally, it should also be emphasized that the different values reported for the σ constants of the p-methoxy group vary a great deal,[34] and the fact that the σ-value used here may not be the correct one may account for the still appreciable deviation observed for p-methoxy-substituted 1,1-diphenylethylene in its reaction with polystyrylcesium, as with this salt an effect based on complexation is presumably very small.

From the pattern of ρ values for the different systems, it may be concluded that the addition of an ion pair (reactions in nonpolar solvents) proceeds essentially by nucleophilic attack of the polystyryl ion pair on the double bond of the monomer and that, as anticipated, the nucleophilic character of an ion pair is substantially lower than that of a free anion (reactions in THF).

This decrease becomes larger for the polystyryllithium ion pair than for the polystyrylpotassium ion pair and even more so than for the polystyrylcesium ion pair ($\rho_{Cs} > \rho_K > \rho_{Li}$).

In principle, the decrease of ρ may be accounted for by two alternative explanations. The most straightforward schemes that can be suggested to represent the addition step of the reaction in nonpolar medium are the following: (1) A direct attack of the ion pair on the monomer

$$P_1^-Alk^+ + M \xrightarrow{k_1} P_2^-Alk^+$$

the rate of which is given by

$$\text{rate} = k_1[P_1^-Alk^+][M]$$

(2) A reversible complex formation of monomer with living polymer followed by a unimolecular rearrangement

$$P_1^-Alk^+ + M \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [P_1^-Alk^+,M] \xrightarrow{k_3} P_2^-Alk^+$$

with two possible expressions for the rate depending on the relative magnitudes of k_3 and k_{-2}.

$$\text{rate} = k_2[P_1^-Alk^+][M] \qquad (k_3 \gg k_{-2}) \qquad \text{(a)}$$

$$\text{rate} = Kk_3[P_1^-Alk^+][M] \qquad (k_{-2} \gg k_3) \qquad \text{(b)}$$

If the reaction proceeds according to the first scheme, the observed rate constant should correspond to the constant k_1, and the Hammett relation may then be expressed by

$$\log k_s/k_0 = \rho\sigma = \frac{E_0 - E_s}{RT} \qquad (1)$$

where E_0 and E_s represent the energy of activation respectively for the reaction with unsubstituted and substituted olefin.

The larger ρ value found in THF ($\rho = \sim 3.2$) compared with that in benzene or cyclohexane ($1.7 < \rho < 2.4$) is accounted for by the fact that a free anion is likely to be more sensitive (ρ) than an ion pair to a change in electron density (σ) of the double bond of the monomer. Similarly, the decrease of ρ observed in benzene for the series Cs > K > Li may be explained in terms of a decrease of the carbanionic character of the respective ion pairs due to increasing field strength of the positive counterion from Cs to Li.

In case (2a), where the complex formation constitutes the rate-determining step, negative values are expected for the Hammett ρ constants, and therefore only case (2b) is considered here. The Hammett equation for the overall rate constant, which is composed of an equilibrium and a true rate constant, is then given by the equivalent form:

$$\frac{E_0 - E_s}{RT} + \frac{\Delta H_0 - \Delta H_s}{RT} = \rho\sigma \qquad (2)$$

It should be stressed that the first term in the left part of this equation should not be compared directly with the $(E_0 - E_s)/RT$ term of the mathematical expression 1 given for the first reaction scheme.

Since formation of the ion pair–monomer complex is now favored by electron-donating substituents (negative σ), the sign of the second term, which is a measure of the ease of complexation, is opposite to that of the first term, and thus the absolute value of ρ should be smaller for the lithium ion pairs than for those with cesium as counterion, for which the effect of complexation may be neglected and the second term in the free energy relationship consequently becomes vanishingly small.

As far as the ρ constant is concerned, both hypotheses, represented by scheme 1 or by scheme 2b, equally well account for the results obtained, and on this basis alone it is therefore not possible to decide whether the propagation reaction in nonpolar solvents proceeds in a single step by direct addition (scheme 1) or occurs in two consecutive steps involving rearrangement of a coordination complex formed in a preliminary step by complexation of the positive counterion with monomer (scheme 2b).

As already stated, the decrease of ρ from Cs to Li observed in benzene could be explained by a decrease of the carbanionic character of the respective ion pairs. If this were the only reason, then it may be questioned why the reactivity of the polystyrylcesium ion pair with respect to the addition of diphenylethylenes in benzene is lower than that of the other ion pairs, a trend in reactivity which is similar to that observed for the homopropagation constants of the ion pairs in the polymerization of styrene. Indeed it is seen that for the free polystyryl carbanion, which is more reactive, the sensitivity to a change in electron density of the double bond is also more pronounced. For the reaction in dioxane, the rate constants decrease from cesium to lithium,[15] and the same order of reactivity probably also holds in THF, at least if the reactivity of only the contact ion pairs is considered.[35] This order is explained by the fact that the coulombic interaction between the two oppositely charged poles of the ion pair, which has to be overcome in the transition state, decreases from Li to Cs, as a result of the increasing ionic radius of the cation. For the reaction in benzene and in cyclohexane, however, the order seems to be reversed, as k_p of the ion pair increases from cesium to potassium and possibly further to lithium.[24] This reversed order may be interpreted as an indication of monomer–cation π-complex formation which lowers the apparent activation energy of the propagation step for the smaller cations and which is prevented in solvating media such as dioxane or THF. Further support of this interpretation is provided by the fact that the ion-pair rate constant for polystyrylcesium is largely independent of the solvent ($k_{p,\text{benzene}} = 18\ M^{-1}\ s^{-1}$;[24a] $k_{p,\text{cyclohexane}} = 19\ M^{-1}\ s^{-1}$ (at 40 °C);[24b] $k_{p,\text{dioxane}} = 24\ M^{-1}\ s^{-1}$;[15] and $k_{p,\text{THF}} = 25\ M^{-1}\ s^{-1}$ [15]). Another strong argument in favor of the complexation hypothesis, in particular for polystyryllithium, can be based on the specific solvent effect upon the reactivity of the polystyryllithium ion pairs, as observed in a study of the propagation of styrene in nonpolar medium in the presence of increasing amounts of THF, where it has been found that at low THF concentrations only reactive monoetherates were present, whereas with increasing THF content, these species were progressively converted into less reactive dietherates.[36] The lower reactivity of the dietherate could be explained in reasonable terms only by assuming that complex formation between the cation and the monomer prior to its addition to the carbanion lowers the apparent activation energy of the propagation reaction, a process which is apparently sterically hindered in the dietherate by the two solvating ether molecules already present.[7]

Conclusion

The above considerations suggest that in the absence of stronger coordinating molecules, complexation of the monomer with the positive counterion constitutes a characteristic feature of the propagation reaction of anionic polymerization in the presence of alkali metals, at least with lithium as a counterion. However, our results do not allow us to describe the exact nature of the complex formed and the role of the cation in the ion pair may well be double in that it reduces the negative charge of the carbanion but also complexes with the monomer.

Finally, it should be noted that the nucleophilicity of the polystyryllithium ion pair in benzene and in cyclohexane is almost identical (Figure 2). At first sight this indicates that an interaction, if there is any, of the cation with the π electrons of the aromatic rings of the solvent has no measurable effect upon the reaction mechanism. Recent results however[36] suggest that there is an interaction between Li^+ cation and the aromatic rings of benzene solvent as well as between the π electrons of the penultimate phenyl ring and those of the phenyl group of the active chain end, the latter effect having the greatest influence upon the reactivity. However, in this work a penultimate unit effect is present both in benzene and cyclohexane and consequently the overall effect is not greatly altered.

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Appendix

For the reaction of polystyryllithium with an excess of *p,p'*-dimethoxy-1,1-diphenylethylene in cyclohexane, it was found that the optical density at the absorption maximum of the newly formed ion pair only slowly decreased after reaching a maximum value, indicating that chain termination resulting from metallation is a rather slow process compared to the addition reaction. Similarly, polystyrylcesium was reacted with an excess of *p,p'*-dimethoxy-1,1-diphenylethylene in benzene, and the progress of the reaction was followed by measuring the decrease of the polystyrylcesium concentration. Analysis of the results was easily accomplished in this case, since the reaction scheme was not complicated by association phenomena as for the lithium analogue,[30] and after making a correction for about 10% of chain termination, it was found that the reaction followed the first-order law, yielding a rate constant which was identical within experimental error with the k_p value obtained before by carrying out the reaction with an excess of the polystyryl salt (Table VI). This again indicates that ring metallation with concomitant chain termination or chain transfer[33] occurs only to a rather limited extent, so that its influence upon the overall rate of addition, especially in the first stages of the reaction, apparently cannot be very important.

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