QUANTITATIVE STUDIES OF ELECTRON-TRANSFER INITIATION OF
POLYMERIZATION

Michael Szwarc

Department of Chemistry (B-014), University of California
San Diego, La Jolla, CA 92093

Abstract - Electron-transfer initiation of anionic poly-
merization involves two steps: electron-transfer from a
donor to a monomer acceptor, yielding monomeric radical-
anions followed by dimerization of the latter. Dimerization
yields dimeric dianions and the respective carbanions
propagate the polymerization. Reaction of the monomeric
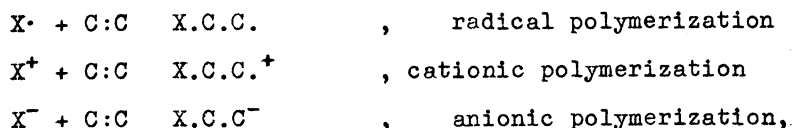radical-anions with unreduced monomer was shown to be of
little significance.
It was shown that the electron-transfer equilibrium is
attained in an extremely short time and the dimerization
is the rate determining step of initiation. The equilibrium
transfer was determined. For conventional homogeneous
donors, e.g., sodium naphthalenide or biphenylide, the
equilibrium is unfavorable in respect to monomer, even
when it is in large excess.
The rate of the dimerization was measured, and it was
shown to depend on the nature of counter-ions. The
numerical results are discussed and a tentative explana-
tion is proposed for the findings.
Heterogeneous electron-transfer initiation is discussed
with emphasis on the adsorption and desorption processes.
The results of some copolymerization are rationalized.

INTRODUCTION

Vinyl, vinylidene or diene polymerization is usually initiated
by addition of some moiety, X, to a monomer ,M, leading to the
formation of a reactive end-group capable of sustaining propaga-
tion. The ensuing polymerization is propagated through a radical,
cationic, or anionic mechanism, depending upon whether X is a radical,
a cation, or an anion. This is shown below:

$$X\cdot + C{:}C \quad X.C.C. \qquad , \quad \text{radical polymerization}$$

$$X^+ + C{:}C \quad X.C.C.^+ \qquad , \text{cationic polymerization}$$

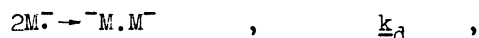$$X^- + C{:}C \quad X.C.C^- \qquad , \quad \text{anionic polymerization},$$

and in each case while one end of a growing polymer is active, the other
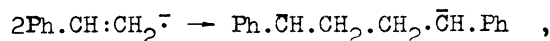remains inert.

An entirely different mechanism of initiation was proposed in the 1950's (Ref. 1), namely, initiation caused by electron-transfer to monomer. An electron transferred from a suitable donor, A or A^-, to a monomer, M, converts it into a monomeric radical-anion
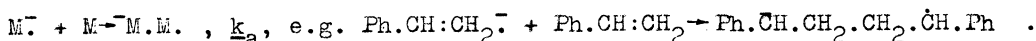
$$A \text{ (or } A^-) + M \rightleftharpoons A^+ \text{ (or } A) + M^- \qquad , K_{tr} \qquad .$$
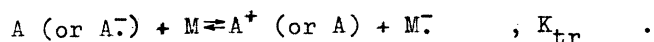
The monomeric radical-anions dimerize into dimeric dianions,

$$2M^- \rightarrow {}^-M.M^- \qquad , \qquad \underline{k}_d \qquad ,$$

e.g. ,

$$2Ph.CH:CH_2^- \rightarrow Ph.\overset{..}{C}H.CH_2.CH_2.\overset{-}{C}H.Ph \qquad ,$$

or react with the available monomer, forming dimeric radical-anions,

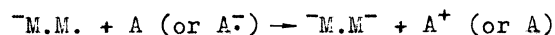$$M^- + M \rightarrow {}^-M.M. \quad , \quad \underline{k}_a, \quad \text{e.g. } Ph.CH:CH_2^- + Ph.CH:CH_2 \rightarrow Ph.\overset{..}{C}H.CH_2.CH_2.\overset{.}{C}H.Ph \quad .$$

The resulting dimeric dianions initiate anionic polymerization propagated from both ends of the macromolecules,

$${}^-M.M^- \overset{M}{\rightarrow} {}^-M.M......M.M^- \quad ,$$

a novel situation leading to valuable consequences. The dimeric radical-anions whenever formed, could perhaps initiate anionic propagation ensuing from one of their ends and simultaneously a radical polymerization from the other. However, this is a highly unlikely event. Most probably, they disproportionate, dimerize, or become reduced to dianions, viz.

$$2^-M.M. \rightarrow {}^-M.M^- + 2M \qquad ,$$

$$2^-M.M. \rightarrow {}^-M.M.M.M^- \qquad ,$$

or

$${}^-M.M. + A \text{ (or } A^-) \rightarrow {}^-M.M^- + A^+ \text{ (or } A)$$
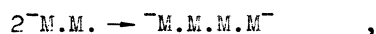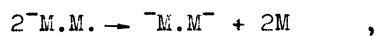
The feasibility of electron-transfer initiation was fully confirmed in subsequent studies. However, its quantitative aspects remained unknown. It is my intention to discuss here this subject and show the methods by which the required information was obtained. In that work flash-photolysis was extensively used, and therefore a few words about the basic feature of this technique are in place. A detailed description of its usage in systems studied by us is given elsewhere (Ref. 2).

Principles of Flash-Photolysis

The experimental set-up is shown schematically in Fig. 1. The approximately 10^{-6} M solution of the active ingredient is introduced into a cylindrical, 10 cm. long quartz cell with optically flat end-windows. The cell is placed between two parallel flash lamps, being surrounded by cuvets containing a UV absorbing solution. A properly collimated beam of monitoring light that passes through the cell is focused on the slit of monochromator. By appropriate setting of the monochromator, one allows the light of the desired wavelength to reach a photomultiplier, and its output is amplified and fed into an oscilloscope.
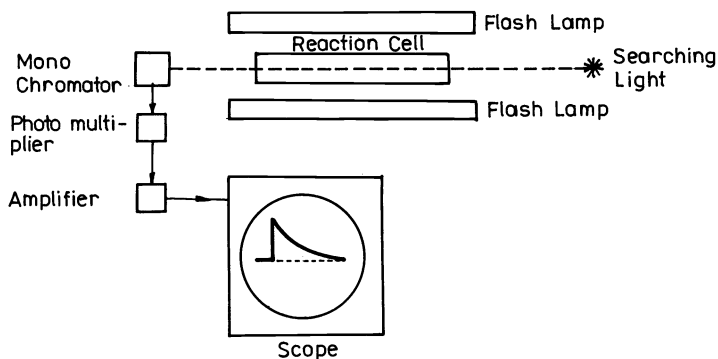
Fig. 1

Triggering the scope, but not the flash lamps, one gets on its screen
a horizontal zero-line, showing how much light of a desired wavelength
passes through the unphotolyzed solution. Subsequently, the flash lamps
are triggered by the scope which has been activated $\sim$100 μsec. earlier.
The ensuing photolysis converts some of the original reagents into
transient species, which react during the dark period following a flash
and eventually yield the final products of the photolysis. The progress
of the dark reaction is revealed by changes in the absorbance of the
monitoring light displayed on the oscilloscope's screen. The resulting
curve gives the intensity of the transmitted light as a function of time.
The systems studied by us were perfectly reversible. At any wavelength
the initially enhanced absorbance or bleaching decayed to a zero-line as
shown in Fig. 1. This observation implies that the transients formed by
photolysis regenerate the original reagents during the dark period of
the reaction. Therefore, flashing could be repeated over and over again,
leaving unaltered the ultimate composition of the photolyzed solution.
By varying the setting of the monochromator, a family of curves is
obtained, each depicting the return of the photolyzed solution to its
original state but monitored at a different wavelength. Such curves
permit one to calculate the optical density of the photolyzed solution
at a chosen time, say 100 μsec. after each flash, and at a desired
wavelength. This, in turn, allows construction of a difference spectrum -
the difference in the absorbance of the transients and the original
reagents at that time.

Quantitative Treatment of Homogeneous Electron-Transfer Initiation

A difference spectrum obtained by flashing a THF solution of dimeric
dianions of α-methyl styrene, $K^+, \bar{C}(CH_3)(Ph).CH_2.CH_2.\bar{C}(CH_3)(Ph), K^+$ =
$K^+, \bar{\alpha}.\alpha^-, K^+$, is shown in Fig. 2 (Ref. 3). Although it fades with
time, its shape remains unchanged indicating that the transients
formed by flash directly regenerate the original dimeric dianions, no
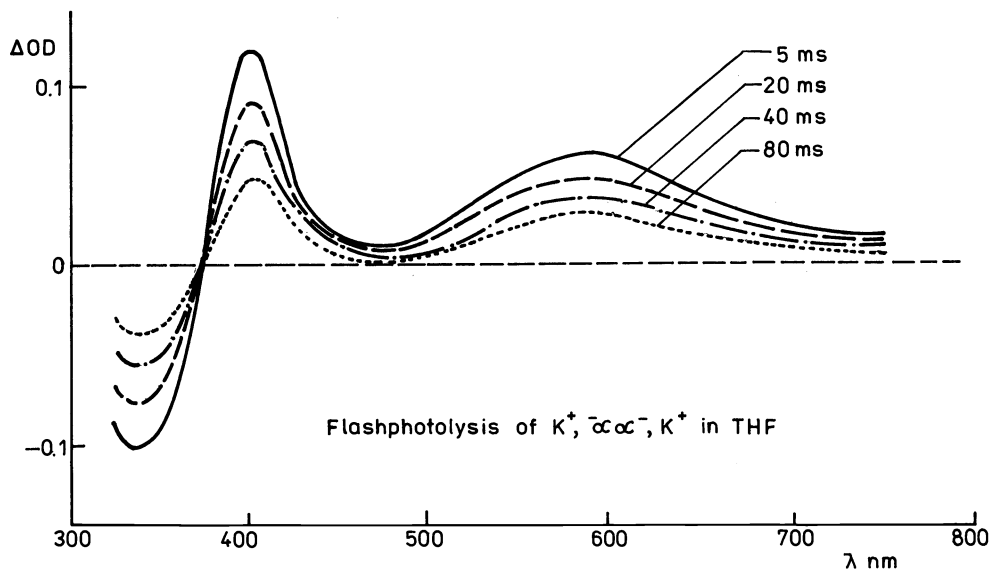other intermediates or products being formed.

Fig. 2

The difference spectrum results from the absorbance of the transient and
bleaching of the dimers. Hence, the spectrum of the transient could be e
constructed by adding the known spectrum of the photolyzed dimers to the
observed difference spectrum. Such a procedure is illustrated by Fig. 3.
The spectrum of the transient agrees with that of $\propto$ -methyl styrene
radical anions obtained by pulse radiolysis and reported by three
independent groups (Ref. 4). One concludes therefore that the dimeric di-
anions of $\propto$ -methyl styrene have been photo-dissociated by flash into
$\propto$ -methyl styrene radical-anions, $\propto.^-$, i.e.

$$K^+, {}^-\!\propto\!\propto^-\ ,\ K^+\ \xrightarrow{h\nu}\ 2K^+,\propto\bar{.}\quad,$$
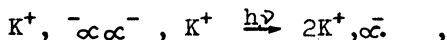
and in the subsequent dark period they dimerized into the dimers.

Analogous studies of flash photolysis of THF solutions of dimeric di-
anions of 1,1-diphenyl-ethylene, Cat^+, $\bar{C}(Ph)_2.CH_2.CH_2\bar{C}(Ph)_2$, $Cat^+ = Cat^+$,
$^-D.D^-$, Cat^+, led to the spectrum of the respective transient shown in
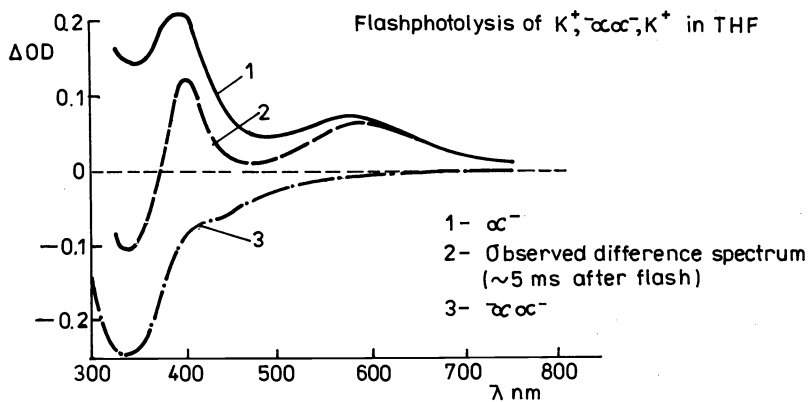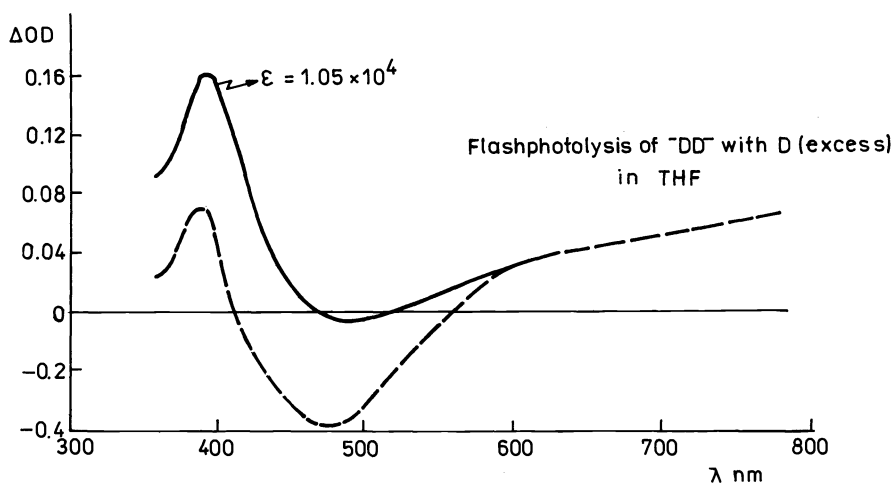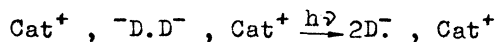Fig. 4 (Ref. 5). Its similarity with the spectrum of 1,1-diphenyl-ethylene

Fig. 3

ΔOD

Fig. 4

radical-anions, $D^{\overline{\cdot}}$, reported by Hamill (Ref. 6) who radiolyzed frozen 2-MeTHF solution of that hydrocarbon, implies that flash-photolysis of those dimeric dianions again leads to their photo-dissociation into the monomeric radical-anions, viz.

$$Cat^+ \text{ , } {}^-D.D^- \text{ , } Cat^+ \xrightarrow{h\nu} 2D^{\overline{\cdot}} \text{ , } Cat^+$$

For both systems reciprocals of Δ optical density are linear with time. For the α-methyl styrene system, this is shown in Fig. 5 where $1/\Delta$ (opt. density) at 340 nm, 400 nm, and 600 nm is plotted vs. time, and for the 1,1-diphenyl-ethylene system in Fig. 6 giving plots of $1/\Delta$ (opt. density) at 390 nm, 470, and 750 nm vs time. Linearity of those plots proves the bimolecular character of processes regenerating the dimeric dianions. Slopes of those plots provide, therefore, the values of the respective dimerization constants, $\underline{k}_d$, divided by $\varepsilon \ell$, where ε is the respective effective molar absorbance and ℓ is the length of the cell. The effective molar absorbances were determined by various methods (Ref. 3,5) and thereafter the dimerization constants of $D^{\overline{\cdot}}$,Cat^+ and $\alpha^{\overline{\cdot}}$, Cat^+ were calculated. Their values, listed in Table I, show their dependence on the nature of cation increasing with its radius. Significantly, the dimerization of radical-anions is substantially slower than of small, neutral radicals, the latter being diffusion controlled, i.e., its bimolecular rate constants are $\sim 10^{10} M^{-1}$ sec^{-1}. Apparently, the repulsion of the negatively charged particles (for free ions) or of the unfavourably oriented dipoles (for ion-pairs) leads to retardation. Surprisingly, $\alpha^{\overline{\cdot}}$,$Cat^+$ dimerize much slower than $D^{\overline{\cdot}}$,Cat^+, an unexplained finding.

Since the dimerization is the rate determining step in the initiation of polymerization by aromatic radical-anions, its rate is

$$\underline{k}_d K_{tr}^2 \left\{ [A^{\overline{\cdot}},Cat^+] \cdot [\text{ monomer}] / [A] \right\}^2$$
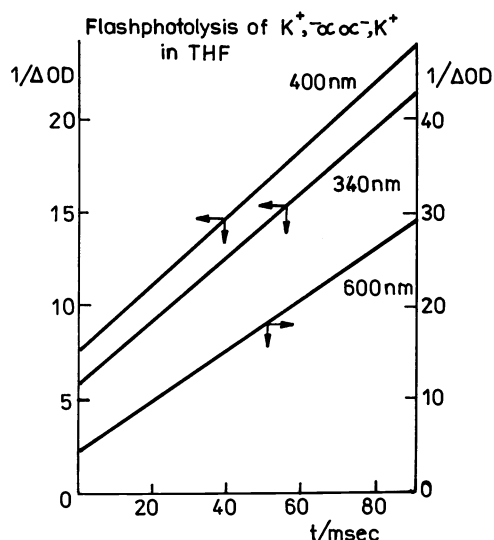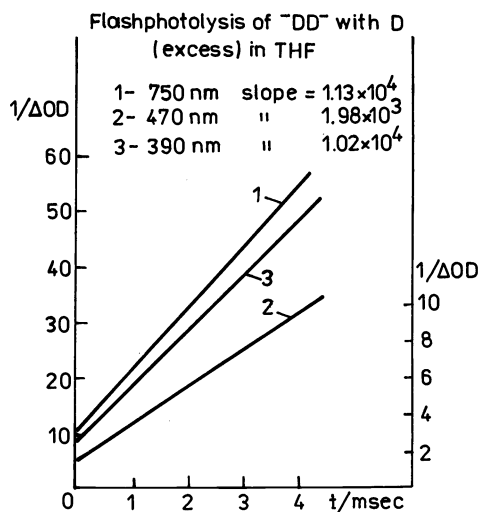
Fig. 5   Fig. 6

Here K_{tr} denotes the equilibrium constant of electron-transfer. Because the relaxation time is extremely short, the equilibrium concentration of the monomeric radical-anions is unperturbed by their dimerization.[x] A numerical example illuminates this point.

Consider the initial conditions of a 1 M THF solution of a monomer containing 10^{-4} M of an initiator $A^{\cdot-},Cat^+$. For as low K_{tr} as 10^{-5}, the electron-transfer equilibrium, established within a few μsec., converts 27% of $A^{\cdot-}$, Cat^+ into monomer$^{\cdot-}$,Cat^+. It takes less than 0.2 sec. to produce 95% of all the dimeric dianions expected in the quantitative conversion, even for as low k_d as $10^6 M^{-1}sec^{-1}$. In that time less than 50 monomer molecules are added to each of the formed growing centers, provided the propagation constant is not larger than 250 $M^{-1}sec^{-1}$ – a rather high value, while at the completion of polymerization 10^4 molecules are added.

The dimerization competes with monomer addition to monomeric radical-anions

$$M^{\cdot-} + M \longrightarrow \cdot M.M^-   , k_a   .$$
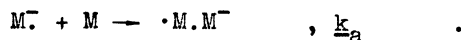
Most likely k_a is smaller than the propagation constant, i.e., $k_a <$ 250 $M^{-1}sec^{-1}$. However, since the concentration of the monomer is at least 10^4 times larger than that of the monomeric radical-anions, the

---

[x]
    This relaxation time is given by $3 = 1/\{k_f [M] + k_b [A]\}$, k_f and k_b denoting the forward and backward rate constants of the electron-transfer. Thus, 3 is at the most 1 μsec.
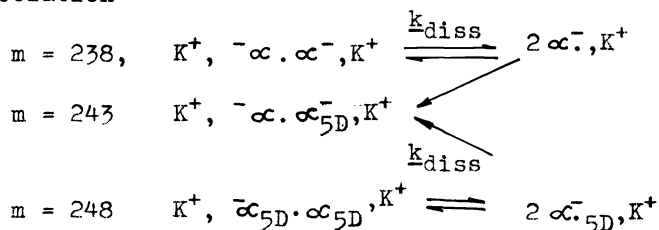
addition competes efficiently with the dimerization. Nevertheless, the resulting dimeric radical-anions, $.M.M^-$, play no role in the polymerization because they are destroyed as soon as formed by the diffusion controlled disproportionation (rate constant $\sim 10^{10} M^{-1} sec^{-1}$). Hence, radical propagation is imperceptible in such systems.

TABLE 1. Dimerization constants of $D^{\overline{.}}, Cat^+$ and $\alpha^{\overline{.}}, Cat^+$ in THF at 25°C

Cat^+	$10^{-8} \underline{k_d} Msec(D^{\overline{.}}, Cat^+)$	$10^{-7} \underline{k_d} Msec(\alpha^{\overline{.}}, Cat^+)$
Li^+	1.2	-
Na^+	3.5	0.2
K^+	10.0	1.0 - 1.2
Cs^+	30.0	-

Dissociation of the dimeric dianions

The dimeric radical-anions are stable. The rate of dissociation of $K^+, ^-\alpha.\alpha^-$, K^+ was determined by the following procedure (Ref. 7): α-methyl styrene perdeuterated in phenyl groups, α_{5D}, was prepared and converted into dimeric dianions, $K^+, ^-\alpha_{5D}.\alpha_{5D}^-, K^+$. Their THF solution was mixed with a solution of ordinary protic dimers, $K^+, ^-\alpha.\alpha^-, K^+$. The reversible dissociation-association

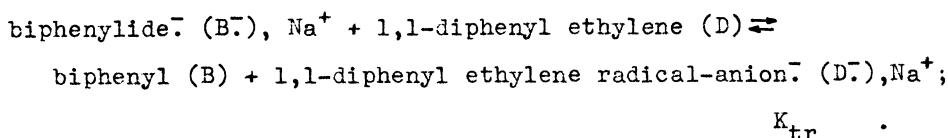$$m = 238, \quad K^+, ^-\alpha.\alpha^-, K^+ \underset{}{\overset{\underline{k}_{diss}}{\rightleftharpoons}} 2\alpha^{\overline{.}}, K^+$$

$$m = 243 \quad K^+, ^-\alpha.\alpha_{5D}^-, K^+$$

$$m = 248 \quad K^+, ^-\alpha_{5D}.\alpha_{5D}^{,K^+} \underset{}{\overset{\underline{k}_{diss}}{\rightleftharpoons}} 2\alpha_{5D}^{\overline{.}}, K^+$$

forms mixed dimers, $K^+, ^-\alpha.\alpha_{5D}, K^+$. For a 50:50 mixture the rate of mixed dimers formation is equal to 1/2 of the rate of the dimer's dissociation, $\underline{k}_{diss}$. To determine this rate the mixture was kept at a constant temperature and at desired time intervals (12h, 24h, etc.) aliquots were removed and protonated by methanol. The resulting hydrocarbons were isolated and analyzed by mass-spectrometer. The analysis gives the fraction, $\underline{f}$, of the homo-dimers, masses 238 and 248, converted into mixed dimers, mass 243, in a predetermined time interval. The plot of $\ln(1-f)$ vs time was linear and from its slope the first order dissociation constant was calculated, i.e., $\underline{k}_{diss} = 6.10^{-8} sec^{-1}$ at 25°C. In conjunction with the determined association constant, this result gives the equilibrium constant of the dissociation, $K_{diss} \sim 10^{-14} M$. Assuming a plausible value of 15 e.u. for ΔS of dissociation, one finds the heat of dissociation $\Delta H \sim 24 kcal/mole$.

Another approach led to the dissociation constant of $Na^+, ^-DD^-, Na^+$ (Ref. 8).
Since 1,1-diphenyl ethylene does not add to its dimeric dianions, a
solution of $Na^+, ^-DD^-, Na^+$ was mixed with radioactive 1,1-diphenyl
ethylene and the kinetics of exchange was investigated. The results led
to the upper limit of the respective dissociation constant, namely
$\underline{k}'_{diss} < 10^{-7}$ sec^{-1}.

The stability of the dimeric dianions should be contrasted with the
lability of the dimeric radical-anions. For example, indirect evidence
reveals that $Na^+, \bar{C}(Ph)_2CH_2CH_2\dot{C}(Ph)_2$ dissociates in a few microseconds,
i.e., its dissociation constant is 10^5-10^6 sec^{-1}.

Electron-transfer equilibrium

Flash-photolysis led also to the determination of electron-transfer
equilibrium constants, e.g.,

> biphenylide$\bar{\cdot}$ (B$\bar{\cdot}$), Na^+ + 1,1-diphenyl ethylene (D) $\rightleftharpoons$
>
> biphenyl (B) + 1,1-diphenyl ethylene radical-anion$\bar{\cdot}$ (D$\bar{\cdot}$), Na^+;
>
> K_{tr} .

This is achieved by flash-photolyzing THF solutions of $Na^+, ^-DD^-, Na^+$ in
the presence of a mixture of biphenyl and 1,1-diphenyl ethylene of a
known composition. Neither hydrocarbon reacts with the dianions, although
both were at much higher concentration than $Na^+, ^-D.D^-, Na^+$. Flash photo-
lysis photo-dissociates some of the dimers into $D\bar{\cdot}, Na^+$ and then equilibrium

$$D\bar{\cdot}, Na^+ + B \rightleftharpoons D + B\bar{\cdot}, Na^+ \quad , \quad 1/K_{tr} \quad ,$$
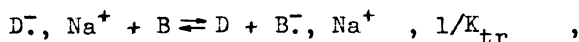
is rapidly established due to relatively high concentrations of B and D
($\sim 10^{-3}$ M). In the dark period following a flash, the photolyzed dimers
are regenerated by the reaction

$$2D\bar{\cdot}, Na^+ \rightarrow Na^+, ^-DD^-, Na^+ \quad , \quad \underline{k}_d \quad .$$
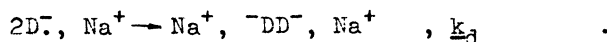
Since $[D\bar{\cdot}, Na^+] = X/(1 + [B]/[D] K_{tr})$, where $\frac{1}{2}$ X is the concentration of
the dissociated dimers,

$$-d(1/X)/dt = \underline{k}_d/(1 + [B]/[D] K_{tr})^2 \quad ,$$

i.e., plots of the reciprocal of the Δ optical density at any chosen
wavelength are again linear with time. However, their slopes give
$\{\underline{k}_d/(1 + [B]/[D] K_{tr})^2\}/\ell\varepsilon$. In the absence of the added biphenyl, an
analogous plot has a slope $\underline{k}_d/\ell\varepsilon$, and hence the ratio of both slopes
gives $(1 + [B]/[D] K_{tr})^2$. Since $[B]/[D]$ is known, K_{tr} is derived from
that experimentally determined ratio.

According to the proposed mechanism, square roots of reciprocals of the
slopes should be linear with $[B]/[D]$ ratio. This is indeed the case
as shown in Fig. 7.

Fig. 7

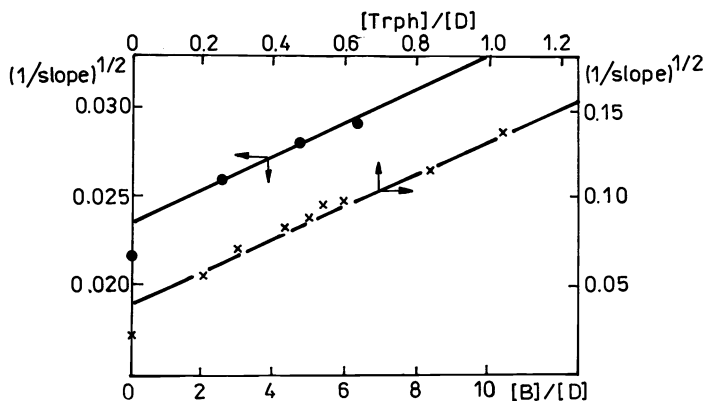This approach could not be adopted in the study of the α-methyl styrene system because K^+, $^-\alpha$, α, α $^-$, K^+ is formed on addition of the monomer to the dimeric dianions, K^+, $^-\alpha\alpha^-$, K^+. However, addition of an excess of biphenyl, B, to a solution of K^+, $^-\alpha\alpha^-$, K^+ changes the character of photolysis, although biphenyl does not react with the dimeric dianions in the dark. In the presence of biphenyl, the transient formed by flash was shown to be its radical-anion, $B^-_\cdot, K^+$. Nevertheless, all the photolyzed dimeric dianions eventually were regenerated in the dark period, but their formation was substantially slower and obeyed a fourth order kinetics, i.e., the reciprocal of Δ (optical density)^3 was linear with time. This is shown in Fig. 8.
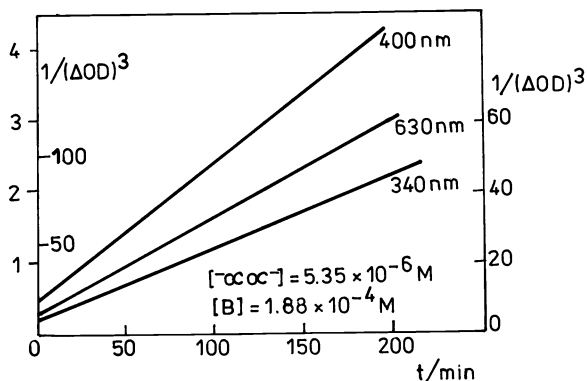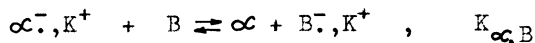

Fig. 8

The basic mechanism discussed in the preceding paragraph accounts for these findings. Virtually all $\alpha^-_\cdot, K^+$ is converted into $B^-_\cdot, K^+$, i.e.,

$$\alpha^-_\cdot, K^+ \ + \ B \rightleftharpoons \alpha + B^-_\cdot, K^+ \quad , \qquad K_{\alpha, B}$$

with $\alpha = B^-_\cdot, K^+$ because $\alpha^-_\cdot, K^+ \ll B^-_\cdot, K^+$ due to the large excess of B. Hence,

$$\alpha^{\bar{\cdot}},K^+ = X^2/K_{B,\alpha} \cdot B$$

where $\frac{1}{2}X$ is the concentration of the photolyzed dimer. Its regeneration is governed by the equation

$$-dX/dt = \underline{k}_d X^4/(K_{B,\alpha} \cdot B)^2 \quad ,$$

i.e., the plot $1/\Delta$ (optical density)^3 is linear with time, its slope being $\frac{1}{3} \underline{k}_d/(K_{B,\alpha} \cdot B)^2$. Since $\underline{k}_d$ is known, $K_{B,\alpha}$ could be calculated from the experimentally determined slope.

Other modes of initiation by radical-anions

Electron-transfer to monomer is not the only mode of initiation caused by radical-anions, although it is unique for non-polar monomers. With some polar monomers, especially cyclic ones, the initiation resembles proto-nation. For example, the reaction of sodium naphthalenide with ethylene oxide follows the route (Ref. 9)
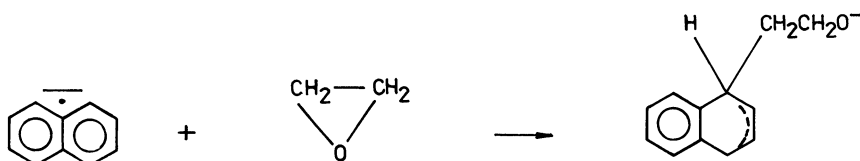
and the reduction of the adduct by the remaining naphthalenide followed by the addition of another molecule of epoxide yields the para or ortho diaduct
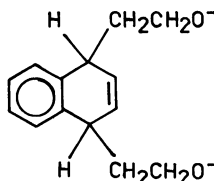

The bimolecular rate constant of the addition of the first molecule of ethylene oxide is ~ 1 $M^{-1}sec^{-1}$ (Ref. 10). The subsequent propagation is due to alkoxide ions. A similar process was reported for the initiation of cyclic-tetra-dimethylsiloxane by naphthalenide (Ref. 11).

The evidence for this mechanism is two-fold: the presence of aromatic moiety in the resulting poly-glycol and the quantitative analysis of the solution left after precipitation of the polymer, demonstrating that only one-half of the utilized naphthalenide was converted into naphthalene.[x]

---

[x]It has been claimed that at very low concentrations of the naphthal-enide, polymers with only one growing group were formed (Ref. 10).Hydrogen abstraction from solvent was proposed as an explanation. However, terminat-ing impurities become significant at very low concentrations of initiators and their action may account for the observations.

Another variant of initiation by naphthalenide was proposed by Sigwalt (12),
who studied the anionic polymerization of propylene sulphide. Formation
of propylene in the course of this reaction led him to the following
mechanism:

sodium naphthalenide + propylene sulphide ⟶

naphatalene + NaS. + propylene
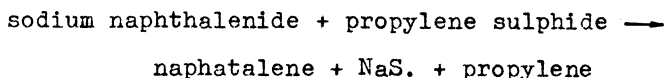
NaS. dimerize and the formed sodium disulphide, NaSSNa, initiates the
propagation. The presence of a S-S bond in the resulting polymer was
claimed in an unpublished report by Boileau and Sigwalt.

Heterogeneous electron-transfer initiation

Reactions of solid alkali metal particles with monomer or its solutions
lead to heterogeneous electron-transfer initiation. The transfer takes
place on the surface of the metal to the adsorbed molecules of the monomer
and yields adsorbed monomeric radical-anions with the positively charged
particles acting as huge counter-ions. Detachment requires not only
desorption of the adsorbed radical-anions but also removal of metal
cations from the metal lattice.

The hindrance of desorption does not affect the mobility of radical-
anions on the metal surface. Hence, their dimerization with formation
of still adsorbed dimeric dianions is very likely, and the latter may
grow and form living oligomers. The degree of polymerization of the
adsorbed oligomers depends on their lifetime on the metal surface, and that
lifetime is shortened by a solvent well solvating cations and therefore
facilitating the desorption that requires removal of the cation from the
metal lattice. This effect is demonstrated by Overberger (13), who
studied the co-polymerization of styrene and methyl methacrylate initiated
by a fine suspension of metallic lithium particles.

Styrene and methyl methacrylate compete for the sites on the metal surface,
the former being favored by the high polarizability of its π electrons.
Hence, only styrene polymerizes on the surface, yielding a block of living
polystyrene. The eventually desorbed living polystyrene initiates poly-
merization of methyl methacrylate in solution because this monomer is
greatly preferred to styrene in anionic polymerization. The greater the
hindrance of desorption, the higher the percentage of styrene in the
resulting block-polymer. Indeed, as demonstrated by the Overberger study,
the size of polystyrene block increased with decreasing solvation power
of the medium and the reactions performed in the absence of ethers yields
co-polymer with 28% of styrene at 1% conversion. On the other hand, the
facile removal of Na^+ cations from the sodium lattice might explain the
formation of homo-poly-methyl-methacrylate in similar experiments involving
sodium dispersion instead of lithium dispersion.

Further evidence of preferential monomer adsorption on a metal surface
is provided by the extensive studies of Richards and his co-workers (14).
Alkyl bromides in tetrahydrofuran vigorously react with alkali metals, say
lithium, yielding the Wurtz coupling products. However, the violent

reaction slows down on addition of aromatic monomers like styrene, and
the nature of the products is drastically changed (Ref. 15). For example,
when an equimolar mixture of ethylbromide and styrene reacts in tetra-
hydrofuran with metallic lithium, the alkyl capped dimer, $C_2H_5.CH(Ph).$
$CH_2.CH_2.CH(Ph).C_2H_5$ forms 90% of the products, about 5% appear as $C_2H_5.$
$CH_2.CH(Ph).C_2H_5$, the remainder being a mixture of an alkyl capped trimer
and butane. The tail-to-tail structure of the capped dimer was demonstrated
by the n.m.r. technique.

It seems that styrene and ethylbromide compete for the sites on the
lithium surface. The adsorption of styrene possessing easily polarizable
𝜋 electrons is more favorable than that of ethylbromide. Hence, Wurtz
coupling is hindered, while the electron-transfer to the adsorbed styrene
yields its radical-anions, and their mobility on the surface allows for
their dimerization. Eventually, the dimeric dianions are desorbed; and
since their reaction with ethylbromide is faster than propagation, the
ethyl capped dimers are the main products.

Further support for the proposed mechanism is provided by the results of
experiments involving phenylbromide instead of ethylbromide (Ref. 16). The
polarizable electrons of this aryl compound allow it to compete
effectively with styrene for the sites on the lithium surface and thus
the Wurtz coupling reaction becomes dominant. Similar results were
obtained with ethyltosylate. Although the reaction of tosylate with living
polystyrene is rapid and quantitative, yielding ethyl capped polymers, its
reaction with the monomer and metallic lithium produces only 10% of the
ethyl capped polymers, the remainder being evolved as butane. Again, the
aromatic nature of tosylate allows it to compete with styrene for the
lithium sites.

An interesting extension of this picture is provided by the behavior of
p-xylylene dibromide (Ref. 17). With butadiene as monomer and tetrahydro-
furan as solvent, their reaction on metallic lithium leads to an unusual
co-polymer,

$$-(BD)_{\underline{n}}-CH_2.C_6H_4.CH_2.CH_2C_6H_4.CH_2-(BD)_{\underline{m}}-\quad (BD\text{-butadiene moiety}) .$$
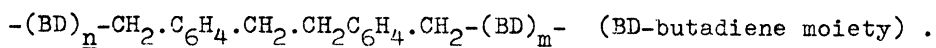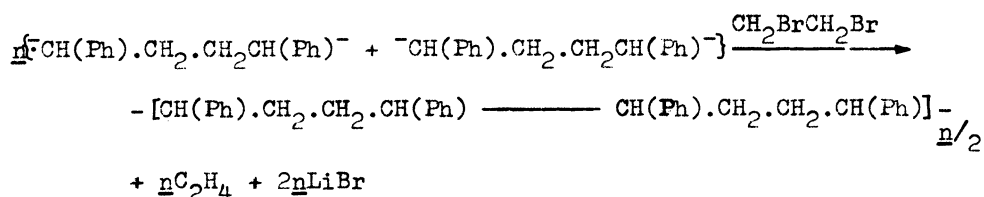
Its composition is determined by the initial ratio of the reagents in the
feed. N.m.r. analysis confirmed the above structure of the aromatic
moieties.

Unexpectedly, the vicinyl dihalides react differently (Ref. 18). For
example, an equimolar mixture of styrene and 1,2-dibromoethane reacts on
lithium metal yielding a head-to-head, tail-to-tail polystyrene, ethylene
and lithium bromide. Apparently, the adsorbed styrene is reduced and
dimerized to the dianions

$$^-CH(Ph).CH_2.CH_2.CH(Ph)^-$$
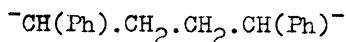
and the latter reacts with the dibromide more rapidly than with the
unreduced styrene, yielding the unconventional head-to-head, tail-to-tail
polymer with elimination of ethylene

$$\underline{n}\{^-CH(Ph).CH_2.CH_2CH(Ph)^- + {}^-CH(Ph).CH_2.CH_2CH(Ph)^-\} \xrightarrow{CH_2BrCH_2Br}$$

$$- [CH(Ph).CH_2.CH_2.CH(Ph) \text{———} CH(Ph).CH_2.CH_2.CH(Ph)] - {}_{\underline{n}/2}$$

$$+ \underline{n}C_2H_4 + 2\underline{n}LiBr$$

Other linking agents were investigated, e.g., dibromo-dimethyl-silane and dichlorophenylphosphine (Ref. 19). Interesting products were obtained with di-epoxides, namely

$$
\begin{array}{c}
^-M.M.CH_2.CH.R.CH.CH_2.M.M.^- \qquad etc., \\
| \quad\quad | \\
OLi \;\; OLi
\end{array}
$$
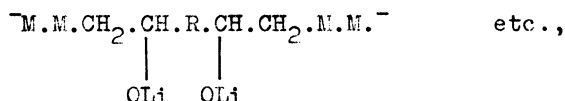
yielding the respective poly-ols on hydrolysis.

Electron-transfer step-wise reaction

One example of such a reaction is discussed. Reaction of bis(1,1-diphenyl ethylene) linked by a chain of aliphatic hydrocarbon yields on reduction with alkali metals or suitable electron donors, e.g., naphthalenide, a product of poly-dimerization. For example:
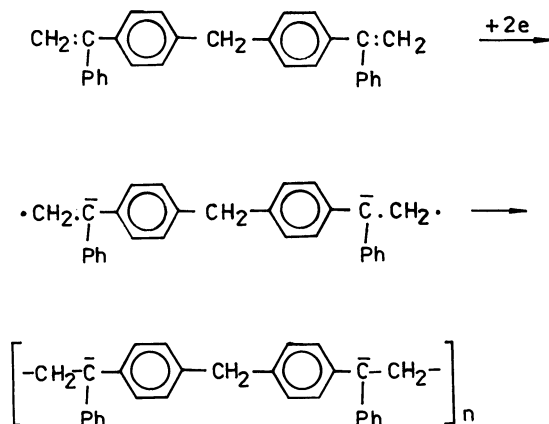
The resulting poly-carbanions are protonated and yield the respective hydrocarbon (Ref. 20). Other examples are provided by the work of Richards and his co-workers, discussed in the preceding section.

REFERENCES

1. a) M. Szwarc, Nature 178 , 1168 (1956); b) M. Szwarc, M. Levy and R. Milkovich, J. Amer. Chem. Soc. 78, 2656 (1956).
2. G. Rämme, M. Fisher, S. Claesson and M. Szwarc, Proc. Roy. Soc. A327, 467 (1972).
3. H.C. Wang, G. Levin and M. Szwarc, J. Phys. Chem. 83, 785 (1979).

4. a) M. Katayama, M. Hatada, K. Hirota, H. Yamazaki and Y. Ozawa,
      Bull. Chem. Soc. Japan 38, 851, 2208 (1965; b) C. Schneider and
      A.J. Swallow, Makromolek. Chem. 114, 155, 172 (1968); c) D.J. Metz,
      R.C. Potter and J.K. Thomas, J. Polymer Sci. A5, 877 (1967).

5. a) H.C. Wang, E.D. Lillie, S. Slomkowski, G. Levin and M. Szwarc,
      J. Amer. Chem. Soc. 99, 4612 (1977); b) E.D. Lillie, S. Slomkowski
      and M. Szwarc, J. Amer. Chem. Soc. 99, 4608 (1977).

6. W.H. Hamill, "Radical Ions", p. 321, E.T. Kaiser and L. Kevan, Eds.
   Interscience (1968).

7. R. Asami and M. Szwarc, J. Amer. Chem. Soc. 84, 2269 (1962).

8. G. Spach, M. Monteiro, M. Levy and M. Szwarc, Trans. Faraday Soc.
   58, 1809 (1962).

9. D.H. Richards and M. Szwarc, Trans. Faraday Soc. 55, 1654 (1959).

10. S. Kazanskii, A.A. Solovyanov and S.G. Entelis, Europ. Polymer J.
    7, 1421 (1971).

11. M. Morton, A. Rembaum and E.E. Bostick, J. Polymer Sci. 32, 530 (1958).

12. a) S. Boileau, G. Champetier and P. Sigwalt, J. Polymer Sci. C16,
       3021 (1967); b) J.P. Favier, S. Boileau and P. Sigwalt, Europ.
       Polymer J. 4, 3 (1968).

13. C.G. Overberger and N. Yamamoto, J. Polymer Sci. B3, 569 (1965); A4,
    3101 (1964).

14. D.H. Richards, Polymer 19, 109 (1978).

15. A. Davis, D.H. Richards and N.F. Scilly, Makromolek. Chem. 152, 121,
    133 (1972).

16. A.V. Cunliffe, N.C. Paul, D.N. Richards and D. Thompson, Polymer 19,
    329 (1978).

17. D.H. Richards and N.F. Scilly, Brit. Polymer J. 2, 277 (1970), 3, 101
    (1971).

18. D.H. Richards, N.F. Scilly, Chem. Comm., p. 1515 (1968),

19. a) D.H. Richards et al., Europ. Polymer J. 6, 1469 (1970);
       b) A.V. Cunliffe, W.J. Hubbert and D.H. Richards, Makromolek. Chem.
       157, 23, 39 (1972); c) D.H. Richards et al. Polymer 16, 654, 659,
       665 (1975).

20. H. Höcker and G. Lattermann, J. Polymer Sci. Symposium 54, 361 (1976).