The Influence of Aromatic Ethers on the Association of the Polystyryllithium and 1,1-Diphenylmethyllithium Active Centers in Benzene

LEWIS J. FETTERS

Institute of Polymer Science, The University of Akron, Akron, OH 44325

RONALD N. YOUNG

Department of Chemistry, The University of Sheffield, Sheffield S3 7HF, U.K.

The influence of diphenyl ether and anisole on the association of the polystyryllithium and 1,1-diphenylmethyllithium active centers has been measured. Severe disaggregation of the polystyryllithium dimers, present in pure benzene, was found to occur at levels of ether addition at which several reliable kinetic studies reported in the literature unequivocally demonstrate a 1/2 order dependence upon polystyryllithium. These results indicate that a necessary connection between the degree of aggregation of organolithium polymers and the observed kinetic order of the propagation reaction need not exist.

The active centers of the polydienyl- and polystyryllithium species, which can be characterized as having polarized covalent carbon lithium bonds, appear (1-8) to form dimeric aggregates in hydrocarbon solvents at concentrations ($<10^{-2}$M) appropriate for polymerization. It is becoming more widely recognized that the kinetic consequences of the aggregation involving carbon-lithium species are but imperfectly understood regarding both the initiation and propagation processes.

It has been known for a considerable time (8,9) that the rates of diene propagation involving the lithium counter-ion in hydrocarbon solvents frequently depend upon the chain end concentration raised to a small power, such as 1/4 or 1/6. It has often been concluded that a small equilibrium concentration of unassociated chain ends is solely responsible for propagation and that the kinetic order of the reaction is a reflection of the extent of active chain end aggregation. The majority of results which seemingly show that the polydienyllithium species are dimeric, would seem to place this attractive kinetic rationalization in jeopardy insofar as the diene systems are concerned.

However, the polymerization of styrene in hydrocarbon sol-
vents has been shown (8,10) to exhibit a 1/2 order dependency on
polystyryllithium concentration. Hence, the concept that only
the unassociated chain ends are reactive may be valid for this
system since association studies have shown (1,2,7,8) that the
polystyryllithium chain ends are associated as dimers. (Szwarc
has stated (11) that polystyryllithium is "probably tetrameric in
cyclohexane." This assessment, though, failed to consider the
light scattering results (7,8) of Johnson and Worsfold).

Several studies have appeared (12,13,14) in which the pro-
pagation reactions involving styryllithium were examined in mixed
solvent systems comprising benzene or toluene and ethers. The
kinetics were examined under conditions where the ether concen-
tration was held constant and the active center concentration
varied. In most cases, the kinetic orders of the reactions were
identical to those observed in the absence of the ether. Thus,
in part, the conclusion was reached (13,14) that the ethers did
not alter the dimeric association state of polystyryllithium. The
ethers used were tetrahydrofuran, diphenyl ether, anisole, and
the ortho and para isomers of ethylanisole.

We have examined the influence of diphenyl ether and anisole
on the association of the polystyryllithium and the 1,1-diphenyl-
methyllithium active centers in benzene solution. The analytical
tool used was the vacuum viscometry method (1,2,3,5) which utili-
zes concentrated solutions of polystyryllithium and the termi-
nated polymer in the entanglement regime. Our results show that
the presence of these ethers can alter the association states of
the foregoing active centers. These findings parallel previous
work (2) involving tetrahydrofuran.

Experimental Section

The procedures used for styrene and benzene purification are
given elsewhere (15) as is the technique used to study the associ-
ation states (1,2,5). The viscometric method relies on the fact
that in the entanglement region, non-polar polymers in solution
and the melt exhibit Newtonian viscosities which are dependent on
$\overline{M}_w^{3.4}$. A compilation of $\eta-\overline{M}_w$ data presented elsewhere (16) re-
veals that for near-monodisperse polymers, the predominant value
of the exponent is 3.4. Furthermore, Doi (17) has recently ex-
tended de Gennes (18) tube model and has shown (17) that $\eta \propto \overline{M}_w^{3.4}$.
The value of the exponent means that even small changes in associ-
ation states can be, in principle, measured with a high degree of
accuracy. The concentrated solution viscosity measurements were
done at 20°C as were the polymerizations. The molecular weights
$(\overline{M}_w)$ of the base polystyrenes used in this work ranged from 1.2x
10^5 to 1.7×10^5 (based on GPC measurements) while the correspond-
ing polymer concentrations ranged from ca. 42 to 30 percent.

The initiator was purified, by distillation (19), sec-butyl-
lithium (Lithco). The ethers and 1,1-diphenylethylene were puri-
fied by sequential exposure to CaH_2, dibutyl magnesium (Lithco)

and polystyryllithium. This purification routine took about one
week to complete. GC analysis, after purification, failed to re-
veal impurities in these compounds. The polymerizations were
conducted in the presence of the ethers with benzene as the sol-
vent. The polystyryllithium active center was converted to the
1,1-diphenylmethyllithium chain end by the addition of ca. 0.1
ml of 1,1-diphenylethylene.

The GPC analysis was conducted using a seven column Styragel
arrangement with tetrahydrofuran as the carrier solvent. Solu-
tion concentrations of 1/8% (w/v) were used. The flow rate was
1 ml min^{-1}. The characteristics of this column arrangement are
presented elsewhere (20,21). The Styragel columns were cali-
brated using eleven polystyrene standards. All of the polysty-
renes prepared in this work were analyzed by gel permeation
chromatography. Without exception, all samples were found to
have values of M_z/M_w <1.07 and values of M_w/M_n <1.05. None of
these samples showed the presence of a low molecular weight tail,
i.e., chromatograms indicating Gaussian distributions were ob-
tained.

Results and Discussion

A potential problem for this work is active center termi-
nation due to reactions with the ethers, i.e., metallation. It
has been reported (13) that polystyryllithium undergoes a moder-
ately rapid termination reaction at 20°C in the presence of ani-
sole or the ethylanisole isomers. These authors, however, did
not recognize that toluene, their solvent of choice, is known
(22,23,24,25,26) to act as a transfer agent in polymerizations
involving alkali metals. (More recent results (27,28,29) have
verified these observations regarding the lithium counter-ion.
n-Butyllithium has also been shown (30) to react with toluene.
In regard to this latter point, Cubbon and Margerison noted (31)
that adding n-butyllithium to toluene led to the formation of
solutions which "developed a yellow-orange color.") If the
spectrum of benzyllithium in toluene in the presence of anisole
resembles that in benzene where the λ max is reported (32,33) to
be 292 nm, the decay in absorbance with time noted (13) at 330
nm may be attributable to transmetallation involving toluene
rather than the foregoing aromatic ethers.

Chain termination proved not to be a problem during the
period over which our measurements were made. This was estab-
lished by the constancy of the absorbance of polystyryllithium
at 334 nm and that of the 1,1-diphenylmethyllithium active center
at 440 nm. Furthermore, the flow times of the solutions were
found to remain constant over the measurement period (ca. 24 hrs.).
An additional indication that chain termination was not a signi-
ficant problem was provided by gel permeation chromatography. As
mentioned previously all of the polystyrene samples exhibited
M_z/M_w and M_w/M_n ratios of 1.07 or less and none of the samples
showed the presence of a low molecular weight tail. This demon-
strates that no detectable chain termination took place during
polymerization.

Figure 1 contains chromatograms of polystyrenes prepared anionically in the presence of anisole and diphenyl ether. The narrow molecular weight distributions of these samples demonstrate that no detectable termination took place during the polymerizations. This lack of a termination step, regarding anisole, is in agreement with the polymerization results (34,35,36,37) where this ether was used as a co-solvent.

The above comments should not be taken as claims that anisole and diphenyl ether cannot be metallated by organolithium species. For example, alkyllithiums are known (38,39,40) to react with anisole, usually in the ortho position. However, these reactions are generally slow, particularly at ambient temperature and when the ether is diluted with a hydrocarbon solvent. Our results merely indicate that active center deactivation via metallation of these aromatic ethers is not a serious problem during the time span of our measurements with species that are, at least, partially delocalized (33).

Table I contains the association values, N_w, for the polystyryllithium and 1,1-diphenylmethyllithium active centers in the presence of diphenyl ether or anisole. The influence on polystyryllithium association by the aromatic ethers is, as expected, less dramatic than observed (2) for tetrahydrofuran (THF) where the value for the equilibrium constant K, of the following, was evaluated to be about 2×10^2;

$$(SLi)_2 + 2nE \xrightleftharpoons{K} 2 (SLi \cdot nE) \qquad (1)$$
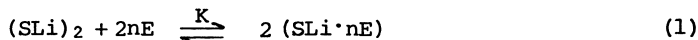
where SLi denotes polystyryllithium and E represents a complexing agent such as an ether. The equilibrium constant can be calculated by the following relation:

$$K = \frac{2(2-N_w)^2 C_0}{(N_w-1) \; E^2 n} \qquad (2)$$

where C_0 represents the total concentration of active centers. As was the case for tetrahydrofuran (2), reasonably uniform values of K for the aromatic ethers were obtained only for the case where n equals one.

The data of Table I shows that anisole has proportionally a greater effect on the association of the 1,1-diphenylmethyllithium active center than does diphenyl ether. This difference may, in part, be due to steric effects involving the latter ether and the 1,1-diphenylmethyllithium active center. Also, data of Table I indicate that the association state of the 1,1-diphenylmethyllithium chain end is nearly two.

Studies have been made (12,13,14) of the kinetics of propagation of styrene under conditions entirely analogous to those described for the measurements of association state. The archetype of this sort of investigation is the classic work of Worsfold and Bywater (10) on the polymerization of styrene by n-butyllithium in benzene. These authors extended (12) their

Table I

The Influence of Diphenyl Ether and Anisole
on the Association of the Poly(styryl) - and
1,1-Diphenylmethyllithium Active Centers

$\frac{[SLi]^a}{10^3}$	$\frac{[DPE]^b}{10^2}$	$\frac{[DPE]}{[SLi]}$	N_w^c	$\frac{K^d}{10^2}$	N_w^e	$\frac{K^f}{10^2}$
1.7			1.98		1.97	
2.1			1.99		1.98	
2.9	6.3	22	1.91	1.3	1.86	3.3
2.1	6.3	30	1.89	1.4	1.82	4.2
2.6	17	65	1.77	1.2	1.69	2.5
2.6	25	96	1.66	1.5	1.59	2.4
1.6	16	100	1.68	1.9	-g-	
1.8	20	111	1.66	1.6	1.58	2.7
2.3	28	122	1.64	1.2	-g-	
2.0	33	165	1.58	1.1	-g-	
1.5	33	220	1.50	1.4	1.41	2.3
1.9	44	232	1.48	1.1	-g-	
	$\frac{[\phi OCH_3]^h}{10^2}$	$\frac{[\phi OCH_3]}{[SLi]}$				
3.3	7.1	22	1.82	5.2	1.65	25
2.7	12	44	1.68	5.6	1.44	27
3.1	18	58	1.61	4.8	1.35	23
2.5	20	80	1.57	4.1	1.29	22
3.0	28	93	1.55	2.8	1.27	15
2.5	25	100	1.56	2.8	1.24	19

[a] Active center concentration.

[b] Diphenyl ether concentration.

[c] Association number for polystyryllithium.

[d] Based on Equation (2) for polystyryllithium.

[e] Association number for the 1,1-diphenylmethyllithium active
center.

[f] Based on Equation (2) for the 1,1-diphenylmethyllithium active
center.

[g] Diphenylethylene was not added to these runs.

[h] Anisole concentration.

work to the situation where tetrahydrofuran was present in ben-
zene solution in constant concentration (10^{-3} molar); a one-half
order dependence of rate upon polystyryllithium concentration was
observed for an ether : lithium ratio over the range 1.2 to 17.5.
In an analogous study, Geerts, Van Beylen and Smets (13) found
that the propagation of styrene also exhibits a one-half order
dependence of rate upon active center concentration when anisole
or 4-ethylanisole was present over the range of [ether]: [lithium]
from 33 to 1030, and also in the presence of 2-ethylanisole for
the range 40 to 3980.

     Comparison of the association numbers found from the vis-
cosity measurements with the invariancy of the kinetic orders
from the value one-half clearly demonstrates the mistake (13,14)
of expecting the existence of a simple and necessary connection
between these two parameters. The assumption (14) that diphenyl
ether does not affect the degree of association of polystyryl-
lithium even at the ratio of 150:1 can be seen to be incorrect.

     A potentially valuable contribution to our understanding of
the generality of a connection between the order of the propa-
gation rate with respect to the organolithium centers might come
from the study of o-methoxystyrene in a hydrocarbon solvent in
the absence of any added ethers or other complexing agents. Smets
and co-workers (41,42) using toluene as solvent reported that
when their results were plotted in the form log rate vs. log
[chain end], "a distinctly curved line was obtained, the order
with respect to the concentration of poly-o-methoxystyrene vary-
ing from 0.67 to 0.51 over a concentration range from 4.5×10^{-4}
(sic) to 1.8×10^{-2} mol/lit" (Table I of ref. 41 shows that the
lowest active center concentration was $5.3 \times 10^{-4} ML^{-1}$). This re-
sult was interpreted as indicating that "at the higher concen-
tration the ion-pairs occur predominantly in the associated form
while increasing amounts of free-ion-pairs are present at lower
concentrations." Scrutiny of their data however, does not pro-
vide convincing evidence that their plot is non-linear. We have
replotted their data (Figure 2); and a least mean squares analy-
sis shows that the gradient is 0.62 and that the relevant corre-
lation coefficient is 0.9994. If there is indeed a connection
between the degree of aggregation and the observed kinetic order,
then it must be concluded that (a) the degree of aggregation is
constant over the concentration range 5.3×10^{-4} to 1.8×10^{-2} molar
and that (b) the number-average mean degree of aggregation, N_n,
is less than two, possibly 1/0.62 i.e., 1.6 (it can readily be
shown that $N_n = 2/(3 - N_w)$ for systems containing near-monodisperse
molecular weight distributions).

     Having assumed that the aggregated chain ends are incapable
of growth, Smets and co-workers (41,42) used a curve fitting pro-
cedure to deduce that the dissociation of the dimeric poly-o-
methoxystyrenyllithium is governed by the constant 10^{-3} molar.
Calculation shows that if this value is correct, the degree of
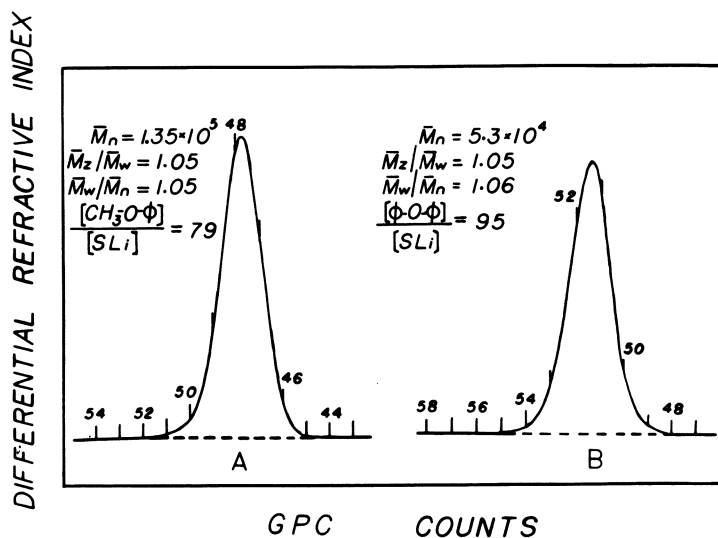dissociation varies from about 0.15 to 0.61 over the range of

Figure 1.   GPCs of polystyrenes prepared in benzene in the presence of anisole (A) and diphenyl ether (B).
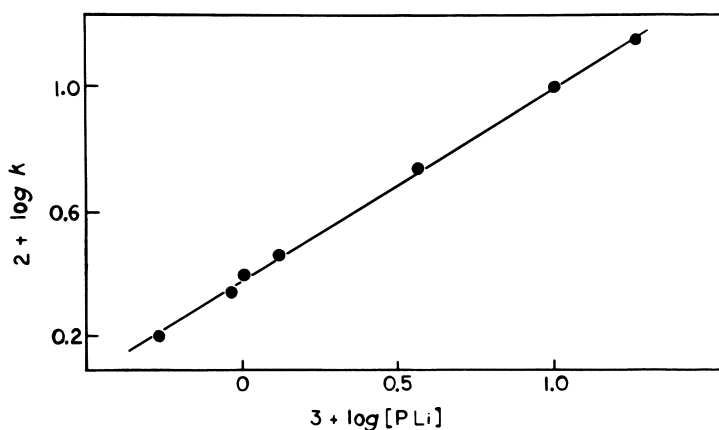

Figure 2.   Polymerization rate vs. active center concentration for 2-methoxystyrene (41, 42).   Rate units are in minutes.

concentration studied. These results are clearly incompatible with those outlined in the preceding paragraph.

In summary, we must conclude that in the case of ether-modified systems based on styrene studied to date, there is no direct relationship between the degree of aggregation and kinetic order in polystyryllithium. There is insufficient reliable data available to draw definite conclusions for reactions carried out in pure hydrocarbons; a fresh study of the polymerization of o-methoxystyrene might shed new light on this situation.

In connection with the subject of the relation between association state and kinetic order, it is germane to mention observations of Roovers and Bywater (45). They measured the dissociation constant for the tetramer ⇌ dimer case for polyisoprenyllithium in benzene. The technique involved a study of the electronic spectra at 272 and 320 nm. If the process they measured can be directly related to the association-dissociation equilibrium, their results can be used to calculate the dissociation constant for the correct dimer ⇌ monomer system. This value is ca. 2×10^{-5} at 30.5°C. If this value is accepted, then the situation is encountered where the degree of dissociation of the polyisoprenyllithium chain ends varies from about 0.10 to 0.62 over a chain end concentration range of 10^{-3} to 10^{-5} molar. However, over this active center concentration range, the kinetic results (44,45, Figure 18 of 15) show a 1/4 order dependency of rate on polyisoprenyllithium. Thus, the polyisoprenyllithium-benzene system is also apparently one where a constant fractional kinetic order is observed even though a variable fraction of the active centers can exist in the unassociated state.

A report has appeared (46) which disputes a preliminary statement of ours (47) regarding the effect of diphenyl ether on the association state of polystyryllithium. This claim (46) was based on only two measurements. We will comment briefly on those measurements. (The authors of that report (46) refer to our work (47) as having been done by "the Akron team" and "the Akron group". No rational justification for the use of that peculiar terminology exists since the first two authors of the preprint in question (47) listed as their affiliation the University of Sheffield. A portion of the work reported in the foregoing preprint (47) has been published, ref. 5 of this paper).

The authors of ref. 46 reported flow times for polystyryl-lithium-benzene solutions before and after the addition of diphenyl ether; whereupon the active centers were terminated and the flow times again measured. Table III of the note in question (46) says that in pure benzene, N_w, is 1.96 and 2.0 — in apparent agreement with the generally held belief that polystyryllithium is exclusively dimeric in benzene. Following the addition of diphenyl ether to achieve the specified concentration (0.15M), the authors in their Table III then reported values of N_w of 1.88 and 1.95 (based on their flow times T_2). From these values, it was concluded that diphenyl ether does not influence the association state of polystyryllithium.

However, the addition of diphenyl ether to achieve the afore-
mentioned concentration is accompanied by an increase in solution
volume of ca. 2.4%, i.e., a decrease in polymer concentration.
The data of Graessley and co-workers (48,49) show that $\eta \propto c^{7.5}M^{3.4}$
(where c denotes polymer concentration) for polystyrene in butyl-
benzene. Thus, the apparently trivial dilution occasioned by the
addition of the diphenyl ether ought to have resulted in apparent
values for N_w of about 2.1 rather than the reported values of
1.96 and 2.0, unless the solution contained some polymer termi-
nated by adventitious impurities. To place this anomaly in
sharper perspective, the results of Graessley, et al.(48,49) pre-
dict that the two average flow times of column 1 (T_1) in Table
III of the note in question (46) should be higher than those re-
ported by about 400 seconds, i.e., 18 and 26% higher than the two
average values reported. This is based on the respective average
flow times of the terminated solutions and the differences in
polymer concentration existing between these active and termi-
nated systems.

If the foregoing assessment is based on the initial flow
times, T_1, then the terminated flow times, T_3, of Table III of
ref. 46, would be about 20 and 15 percent lower than the values
listed. Thus, the association data given by these authors (46)
do not accurately reflect the concentration change brought about
by the addition of diphenyl ether.

The data of Tables II and III of ref. (46) also show (48,49)
that the viscosities of the four polystyryllithium solutions
possessed viscosities ranging from about 3×10^3 to 1.7×10^5 poise
with three of these systems having viscosities greater than ca.
3.0×10^4 poise in the evacuated Ubbelohde viscometers needed for
these measurements. Solutions with viscosities in the range of
10^3 to 10^5 poise do not lend themselves to accurate flow time
measurements due to difficulties in filling the viscometer bulb,
the very slow rate of flow of these solutions between the fidu-
cial marks, and drainage problems, viz, the adherence of the
polymer solution to the viscometer interior. These problems are
not avoidable by the use of large diameter (>1 cm) tubing.
Hadjichristidis and Roovers (50) used Ubbelohde viscometers to
study concentrated polyisoprene solutions and concluded that in
practice the technique is limited to systems having viscosities
less than 10^3 poise. (Unless the solutions are driven by an in-
ert gas). Our experience is entirely in concordance with this
assessment, as is that of others (51).

Finally, two comments made (46) in reference to our prelim-
inary statement (47) should be assessed:

(a) "Purified, and not commercial, ether has to be used,
otherwise some carbanions are destroyed." Our purification pro-
cedure is presented in the experimental section of this paper.
The implication that we would use an unpurified ether is an un-
called for invention of the authors of ref. 46.

(b) "Prolong (sic) action of the ether gradually destroys
the carbanions as revealed by the decrease of optical absorption
at 344 nm." We wish to note that this termination reaction seems
not to have influenced the viscosity results of Wang and Szwarc
(46) nor those of Yamagishi and co-workers (14) where species
analogous to diphenyl ether were used. These authors (46) seem,
though, to imply that termination has influenced our results re-
garding diphenyl ether. We have, as noted, considered this possi-
bility in our work.

In summary, we wish to suggest that in the case of the tetra-
hydrofuran and aromatic ether modified systems based on styrene
studied to date, there does not appear to exist a direct relation-
ship between the mean-degree of active center association and
kinetic order. We do not mean, with this assessment, to imply or
claim that the concept that only the unassociated active centers
of polystyryllithium in hydrocarbon solvents are the active en-
tities is incorrect. However, our association results (this work
and ref. 2), combined with the available kinetic findings for
these ether modified polymerizations, seemingly indicate that re-
action orders need not necessarily yield direct insight into the
states of active center association. In our opinion, greater
understanding of the apparent complex nature of these organoli-
thium based reactions will be forthcoming by a more judicious
approach to the identification of the active centers in these
polymerizations; and approach, which in effect, was advanced by
Brown some years ago (52,53). Along this line, Kaspar and
Trekoval (54,55) have concluded from their kinetic analysis that
styrene can react directly with the polystyryllithium dimer in
benzene solution.

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