positive slope (≈ 4.0 eV^{-1}) expected from a model in which the quencher acts as an electron donor.[7] Curvature seems to occur, again as expected, when k_Q approaches the diffusion limit. (3) Data points for arene–fumaronitrile (FN), phenanthrene(P)–dimethyl fumarate (F), and 9-cyanophenanthrene (9CNP)–diethylaniline (PhNEt$_2$) exciplexes cluster together and are well represented by the leftmost line. These exciplexes are quenched ($k_Q \approx 10^8$ M^{-1} s^{-1}) even when ΔE_Q is negative (≈ -0.6 eV). (4) The pyrene excimer and the 9CNP–*trans*-anethole (*t*-An) and 9CNP–*p*-butenylanisole (*p*-BA) exciplexes are far less quenchable. The single line which correlates data for these quite different complexes is shifted by about $+1.0$ eV from the leftmost line. These cases require positive ΔE_Q ($+0.4$ eV) for modest quenching rates ($k_Q \approx 10^8$ M^{-1} s^{-1}). (5) The "heteroexcimer" 9CNP–3,6-dimethoxyphenanthrene (3,6MeO$_2$P) fits an intermediate line.

The common slope for all data points suggests a common charge-transfer mechanism for both exciplex and excimer quenching.

$$D_Q + (D^{\delta+} \cdots A^{\delta-})^* \rightarrow (D_Q^{\delta+} \cdots D \cdots A^{\delta-})$$
$$\rightarrow D_Q \cdot^+ + D + A \cdot^-$$
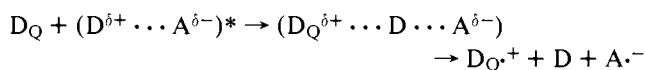
Termolecular photochemistry may be expected to result from the radical ions $D_Q \cdot^+$ and $A \cdot^-$. The unsymmetrical geometries, previously demonstrated[8] for one emissive *exterplex*, and which we have suggested[1a] as being likely for the quenching interaction are easily rationalized. If D_Q is to perturb χ_2, the site of interaction should be at D where χ_2 is predominantly located.

Failure of a single line to correlate all data is, we believe, due to the failure of ΔE_Q as an approximation to $\Delta E_Q'$. We note that the exciplexes which are quenched even when ΔE_Q is negative have large ($\gtrsim 1.5$ eV) HOMO$_D$–HOMO$_A$ (ΔE_{HOMO}) energy gaps. ΔE_{HOMO} is, however, small (<0.8 eV) for the group which requires positive values of ΔE_Q for efficient quenching. The single "heteroexcimer" is an intermediate case ($\Delta E_{HOMO} = 1.04$ eV). When ΔE_{HOMO} is large ($\gtrsim 1.5$ eV) exciplex binding must surely be exclusively CT with D consequently electron deficient and χ_2 located almost exclusively on it. Presumably, χ_2 is then like the HOMO of D$\cdot^+$. The essentially unit positive charge must *lower* χ_2 relative to HOMO$_D$, leading to $\Delta E_Q' \gg \Delta E_Q$ and the observation of quenching even for values of ΔE_Q down to about -1.0 eV. Since χ_2 lies *below* HOMO$_D$, we predict the excited monomer (D*) will be quenched less efficiently than the exciplex (D$\cdots$·A)* by a given D_Q. This appears to be the case, for example, $k_Q \approx 5 \times 10^6$ M^{-1} s^{-1} for quenching of phenanthrene fluorescence by 2,3-dimethyl-2-butene whereas $k_Q = 1.6 \times 10^9$ M^{-1} s^{-1} for quenching[1a] of the P–FN exciplex by the same donor.

When ΔE_{HOMO} is small ($\lesssim 0.8$ eV), χ_2 is a combination of HOMO$_D$ and HOMO$_A$ with the energy of χ_2 *above* that of HOMO$_D$ as predicted by the simple FMO model (Figure 1). Here $\Delta E_Q' < \Delta E_Q$ and the quenching is less efficient than is predicted from values of ΔE_Q. Since χ_2 lies *above* HOMO$_D$ we expect D* will be quenched more efficiently than (D$\cdots$A)* by a given D_Q. This also seems to be the case, for example, $k_Q \approx 5.9 \times 10^7$ M^{-1} s^{-1} for quenching of the pyrene excimer by diethylaniline whereas $k_Q = 6.2 \times 10^9$ M^{-1} s^{-1} for quenching of pyrene monomer fluorescence by the same donor.

The FMO rationale above should be applicable, mutatis mutandis, to acceptor quenching also. We have performed a few experiments with acceptors as quenchers. Correlation is hampered by the difficulty of obtaining electron affinities. The estimates obtained from Ip-Es (the singlet excitation energy) suggest $\Delta E \sim 1 \rightarrow 1.5$ eV is required for acceptor quenching at $k_Q \approx 10^9$ M^{-1} s^{-1}, but further data are required before more dependable predictions can be made.

Our results lead to reasonable predictions of donor quenching rates for *any* singlet exciplex. The utility of the exciplex quenching method for exploring the role of exciplexes in photochemical reactions is thus greatly enhanced.

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David Creed,*[9] Richard A. Caldwell
Hiroyuki Ohta, D. C. DeMarco
Department of Chemistry, The University of Texas at Dallas
Richardson, Texas 75080

The Utilization of a Polymeric Phenylthiomethyllithium Reagent for the Homologation of Alkyl Iodides and Its Application for the Study of Intraresin Reactions of Polymer-Bound Functional Groups

Sir:

The concept that lightly cross-linked polymer matrices are perfectly rigid and inflexible is no longer acceptable. In recent years it has been demonstrated that polystyrene chains cross-linked with several percent divinylbenzene have the capability for very significant internal mobility[1] thus permitting polymer-bound functional groups to undergo intraresin reactions.[2] Nevertheless, there are a number of intriguing reports that suggest restricted interaction of polymer-bound functional groups can be achieved under certain conditions.[3] Such conditions include (1) higher levels of cross-linking,[3b,d,f] (2) very low degrees of polymer substitution,[3a,e] (3) lower reaction temperatures[3a] and, possibly, (4) the clustering of charges located near the polymer backbone.[3c] Evidence in support of the latter two factors is very limited.

We became interested in the possible role of charge clustering and temperature in controlling the interaction of polymer chains after observing the selective monooxidation of 1,7-heptanediol with a polymeric thioanisole reagent.[3e] Although the results clearly demonstrated that selective formation of the monohydroxyaldehyde increased with lower concentrations of polymer-bound functional groups, it was not possible to assess the influence of the relatively low reaction temperature or the clustering of ionic groups on the observed selectivity. Thus, temperatures approaching the glass transition temperature might be expected to result in relatively rigid polymer chains as observed in the dry state,[4] while the devel-

Table I. Reaction of the Insoluble Phenylthiomethyllithium with 1,4-Diiodobutane. Conversion to Higher Homologues

Reaction no.	Sulfide concn [mequiv/g]	Polythioanisole mmol of S [mequiv of S per idodide]	Starting $I\text{-}(CH_2)_4\text{-}I$ (mmol)	Additional reagents added [a]	Reaction temp(°C)/ time(h) [b]	Unreacted $I\text{-}(CH_2)_4\text{-}I$ [c] (mmol)	Products [d] Total mmol [e]	Ratio of diiodides 1,4	Ratio of diiodides 1,5	Ratio of diiodides 1,6
1	0.87	1.24 [1.04]	0.597	DABCO [2.14]	−30/3	0.138	0.223	17	19	64
2	1.85	1.07 [1.06]	0.503	DABCO [1.79]	−30/3	0.156	0.176	15	14	71
3		1.04 [1.04]	0.501	DABCO [1.65]	−70/5	0.351	0.071	32	33	35
4		1.40 [1.82]	0.384	—	−70/3	0.090	0.180	49	25	26
5		1.32 [1.91]	0.345	CuI [1.61] [f]	−70/3	0.222	0.087	49	24	27
6		1.14 [1.83]	0.311	—	−70/3, 0° → RT/O.N.	—	~0.2	21	8	71
7	Monomer	1.90 [2.07]	0.513	—	−70/3	—	0.493	15	65	20
8		1.28 [2.13]	0.300	—	−70° → RT O.N.	—	0.200	0	23	77

[a] After the lithiated beads were washed with THF at −70 °C, DABCO or cuprous iodide was added unless noted otherwise. [b] Refers to reaction of polymeric phenyllithium with 1,4-diiodobutane. The reaction was terminated by addition of MeOH. [c] Corresponds to amount of unreacted starting material in solution phase (footnote d) after termination of reaction. [d] Products obtained by two-step sequence were determined by GLC (4% QF 1, 120 °C) using tetradecane as an internal reference. Integration factors of diiodides to tetradecane were 1.28, 1,4; 1.30, 1,5; and 1.32, 1,6, respectively. [e] Less than quantitative conversion of polymer-bound intermediates to product presumably accounts for missing material. [f] After addition of CuI, the mixture was stirred for 1 h at −50 °C.

Table II. A Comparison of the Oxidation of 1,7-Heptanediol with the Homologation of 1,4-Diiodobutane via Polymeric Thioanisole Derived Reagents

[1] Oxidation of 1,7-Heptanediol

| % cross-linking	Sulfide concn [mequiv/g]	Equiv of S per hydroxyl	Reaction time (h)	Reaction temp (°C)	Ratio of products (%) S.M.	Ratio of products (%) CHO	Ratio of products (%) [CHO]₂
3	~7−8% Subst. [0.66]	1.0	6	−25	47.6	50.2	2.2

[2] Homologation of 1,4-Diiodobutane

% cross-linking	Sulfide concn [mequiv/g]	Equiv of S per iodide	Reaction time (h)	Reaction temp (°C)	Ratio of products (%) S.M.	Ratio of products (%) 1,5	Ratio of products (%) 1,6
3	~10% Subst. [0.87]	1.0	3	−30	17	19	64

opment of ionic clustering can be likened to a form of increasing cross-linking.[5] In an attempt to evaluate the effect of these variables on reaction selectivity, we elected to study an additional application of the polymeric thianisole reagent at moderate levels of polymer substitution.
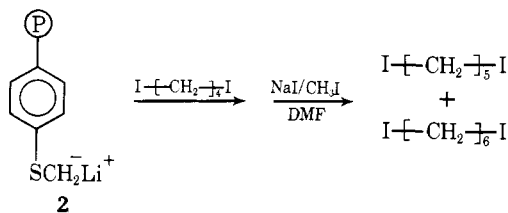
The procedure for homologating alkyl iodides with phenylthiomethyllithium, as originally developed by Corey,[6] appeared to offer promise as an applicable experimental system. A polymeric form of phenylthiomethyllithium, 2, was prepared[7] by treatment of the insoluble thioanisole reagent[3e] 1 (1.85 mmol/g) with 3 equiv of n-butyllithium in THF–DABCO (0 °C, 2 h). The resulting anion was then cooled to −70 °C and treated with an excess of 1-iodooctane (2 h, −70 °C, O.N., room temperature), filtered washed, and dried. Further treatment of the intermediate thioether 3 with excess CH₃I/NaI in dry DMF (20 h, 75 °C bath) produced the anticipated 1-iodononane in 82% yield (based on polymer 1 as the limiting reagent). The polymeric thioanisole is regenerated in the process.

It was anticipated that a similar use of 1,4-diiodobutane would provide an appropriate system for the study of intraresin
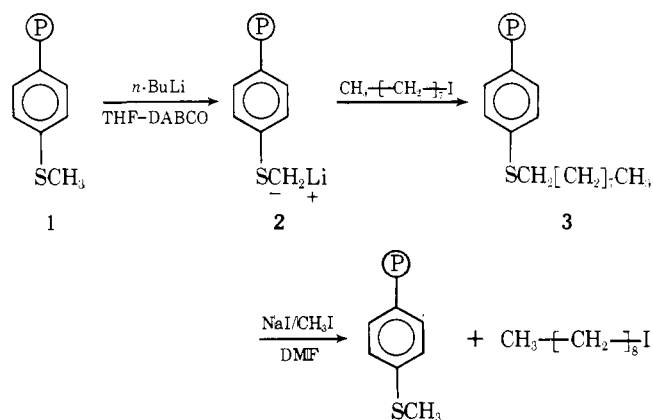
reactions of polymer-bound ionic functional groups at low temperatures.[8] Thus, the ratio of 1,5- to 1,6-diiodoalkanes obtained by the two-step homologation sequence would be a direct indication of the interaction of reactive sites.

The results of a variety of experiments utilizing both mo-

nomeric and polymeric[7] forms of phenylthiomethyllithium are shown in Table I. Interestingly, the use of a polymer with ca. 22% ring substitution (reaction 2; 1.85 mequiv of S/g) produced a high preponderance of the product (1,6-diiodohexane) resulting from reaction at both terminal iodides. A lower concentration of functional groups (reaction 1, 0.87 mequiv of S/g, ca. 10% ring substitution) again failed to provide a selective reaction at only one of the terminal iodides. In addition, the use of a lower bath temperature (reaction 3), increased number of equivalents of sulfide (reaction 4), or the utilization of a copper derivative[9] (reaction 5) all resulted in the formation of nearly equal amounts of the $n + 1$ and $n + 2$ homologues of 1,4-diiodobutane. A control reaction with phenylthiomethyllithium (reaction 7) run under the same conditions of temperature and concentration as several of the polymer runs resulted in a high yield of products, with the major component being 1,5-diiodopentane. Comparison of longer reaction times for both the monomeric and polymeric phenylthiomethyllithium reagents (compare reactions 6 and 8) indicated a marked similarity of product ratios except for the presence of significant amounts of starting material common to most of the experiments utilizing the polymeric reagent.[10] It is clear from the results presented in Table I that extensive interaction of polymer-bound functional groups is occurring under these conditions.

An interpretation of these results can be formulated from a comparison of the homologation of 1,4-diiodobutane with the previously reported[3e] oxidation of 1,7-heptanediol as displayed in Table II. A number of similarities can be drawn between the two transformations: (1) the fact that both polymeric reagents are prepared from the same insoluble thioanisole,[7] (2) the same level of cross-linking is present, (3) both reactions utilize solvents with similar swelling properties for the matrix,[1c,d] (4) the concentration of polymer functional groups is nearly the same, (5) the same equivalents of sulfide are employed in each case, (6) reaction times and temperatures are comparable, and (7) overall conversion to products is similar. *Surprisingly, the selectivities appear to be reversed.* The reaction employing polymeric phenylthiomethyllithium results in a preponderance of site interaction, while the evidence obtained for the oxidation of 1,7-heptanediol via the chlorosulfonium reagent **4** (see Table II) indicates significant site isolation.[11]

Polymers bearing anionic groups bound to the backbone (i.e., styrene–acrylate copolymers) have been shown to exist in solution with extensive ionic clustering.[5] The presence of such domains would be expected to lead to restricted mobility of polymer chains,[5] while simultaneously providing regions of high concentrations of functional groups. Similar behavior of the insoluble phenylthiomethyllithium **2** might therefore be expected to resemble concentrated solutions of reactants, thus leading to extensive interaction of polymer-bound functional groups, even with fairly low polymer substitution. Lower reaction temperatures should assist this behavior. Conversely, it is reasonable to assume that positively charged functional groups bound to the polymer backbone will not be induced into forming charge clusters through the agency of a counterion such as chloride, but rather lead to an extension of polymer chains due to repulsion of like charges.[12] Thus, the chlorosulfonium polymer **4** will provide an environment for site isolation,

when the concentration of these sites is not too high. Lower temperatures should also assist such behavior.

Even though lightly cross-linked polymer chains have the capacity for significant mobility in the swollen state, our results emphasize the necessity to further consider the interaction of polymer-bound functional groups in light of individual reaction conditions and mechanism. The presence of charged sites can have pronounced effects as shown above. Other studies suggest that polymer transformations leading to increased levels of covalent cross-linking (i.e., chloromethylation) will result in reduced mobility of polymer chains.[2,13] Still other investigations have shown that polymer chain mobility is affected by the swelling capacity of the reaction media.[1c,d] Low reaction temperatures and concentrations of polymer-bound functional groups can be expected to enhance the apparent isolation of reactive sites. Thus, the interaction of polymer chains can be controlled under appropriate conditions.

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(8) The reaction of 1,4-diiodobutane with **2** was carried out under slightly different conditions. Prior to reaction with 1,4-diiodobutane, **2** was washed free of excess *n*-BuLi at −70 °C, followed by the addition of fresh solvent containing appropriate reagents such as DABCO or CuI. The reaction with 1,4-diiodobutane was terminated by addition of MeOH. Washings of the resulting resin were examined for unreacted starting material by GLC. The absence of any 1,5- or 1,6-diiodo product at this point in the reaction sequence was also confirmed by GLC.

(9) The disappearance of suspended copper(I) iodide and the development of brownish gray coloration in the polymer beads were taken as strong evidence for the formation of a polymer bound copper reagent.

(10) The failure to consume all starting material is probably due to the inaccessibility of a portion of the "reactive" sites.

(11) As additional support for this conclusion we have found (unpublished results) that an oxidation of 1,7-heptanediol conducted with the thioanisole–chlorine complex under conditions identical with the polymer version given in Table II produced 5.2% of the monoaldehyde and 37.9% of the dialdehyde, along with 4.5% starting material and 52.4% of a mixture of chlorides.

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(14) Dynapol postdoctoral fellow 1975–1976.

Guy A. Crosby, * **Masao Kato**[14]

Chemical Synthesis Laboratories, Dynapol
Palo Alto, California 94304

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The Similarity of Solvent Effects on Carbocations[1]

Sir:

Evidence is accumulating which suggests that the relative energies of simple,[3] isomeric secondary and tertiary carbonium ions are similar in the gas phase and in solution.[4–6] Specifically,