$$Ph_3C^+ \xrightarrow{h\nu} {}^1(Ph_3C^+)^* \rightarrow {}^3(Ph_3C^+)^*$$

$$PH \xrightarrow{{}^3(Ph_3C^+)^*} P\cdot \rightarrow P_n\cdot + P_m$$

The details of this reaction are now under investigation: for example, the change of absorption spectra during photoirradiation, laser photolysis of this system, and experiments using other triphenylmethyl derivatives such as Ph_3CBr and $Ph_3CS_nCl_5$. They will be reported later.

Acknowledgment. The authors wish to thank Professor M. Nagasawa and Dr. T. Kitano of Nagoya University for a supply of standard PMSt samples for GPC measurements.

References and Notes

(1) E. E. van Tamelen and T. M. Cole, Jr., *J. Am. Chem. Soc.*, **93**, 6158 (1971).
(2) D. M. Allen and E. D. Owen, *J. Chem. Soc., Chem. Commun.*, 848 (1971).
(3) T. M. Cole, Jr., *J. Am. Chem. Soc.*, **92**, 4124 (1970).
(4) E. E. van Tamelen, T. M. Cole, R. Greely, and H. Schumacher, *J. Am. Chem. Soc.*, **90**, 1372 (1968).
(5) F. Subira, A. Polton, and P. Sigwalt, International Symposium on Cationic Polymerization, Rouen, 1973, No. 36.
(6) C. Capellos and A. O. Allen, *J. Phys. Chem.*, **73**, 3264 (1969).
(7) H. Sakurai and K. Mochida, *Bull. Chem. Soc. Jpn.*, **49**, 3703 (1976).
(8) H. Yamaoka, T. Ikeda, and S. Okamura, *Macromolecules*, **10**, 717 (1977).
(9) T. Ikeda, H. Yamaoka, and S. Okamura, manuscript in preparation (presented in part at 26th IUPAC Congress, Tokyo, 1977).
(10) (a) Department of Polymer Chemistry; (b) Research Reactor Institute.

Tomiki Ikeda,*[10a] Hirokazu Shimizu,[10a]
Hitoshi Yamaoka[10b] and Seizo Okamura[10a]
Department of Polymer Chemistry, Faculty of Engineering,
Kyoto University, Kyoto 606, Japan,
and Research Reactor Institute,
Kyoto University, Kumatori 590-04, Osaka, Japan

Received May 31, 1977

Influence of Solvent on Site Isolation in Polystyrene Resins[1]

We have previously shown that the degree of swelling of cross-linked polystyrene as defined by the swelling solvent has a large influence on the mobility of nitroxide free radicals covalently attached to and imbibed in the support.[2] Although these data help define the physical properties of pendant groups and imbibed molecules they do not, as others have suggested,[3] provide direct information concerning polymer chain mobility nor do they bear directly on the question of how insulated molecules are from one another when placed along a polystyrene backbone at low concentrations, i.e., site isolation.

Due to the intense interest that presently centers around site isolation techniques[3–7] and due to the rather indiscriminate use of swelling solvents, we felt that it was important to obtain data which would either support or dispel the notion that the degree of swelling influences site–site interactions in cross-linked polystyrene and we now wish to report pertinent findings.

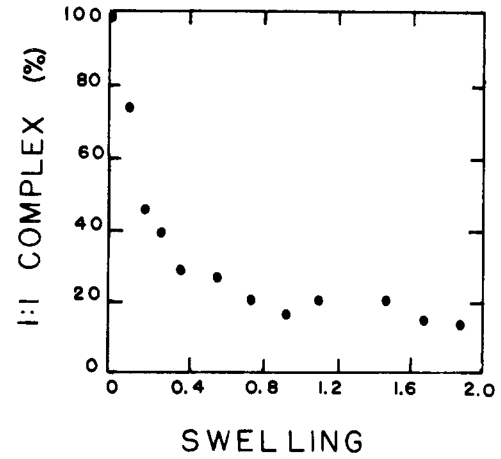
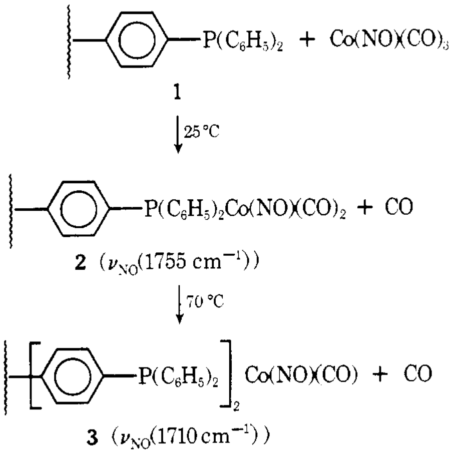


Figure 1. Plot of percent of 1:1 complex remaining as a function of degree of swelling, g of *m*-xylene/g of dry resin, of **2** after a reaction time of 240 h at 70 °C as estimated through relative IR band intensities.[16]

In order to study site isolation we have employed a method introduced by Collman which consists of infrared measurements of 1:1 and 2:1 complexes formed between poly(styryldiphenylphosphine) and $Co(NO)(CO)_3$.[8] Polystyryl–diphenylphosphine **1** was prepared from cross-linked polystyrene (Biobeads SX-2, 2% DVB, 200–400 mesh) by sequential bromination (Br_2,BF_3), lithiation (*n*-BuLi, THF), and treatment with $(C_6H_5)_2PCl$ using procedures previously described[9] and contained 1.1 mmol of phosphine/g (14% ring substitution). Treatment of 2 equiv of **1** with a benzene solution of 1 equiv of $Co(NO)(CO)_3$ for 24 h at 25 °C yielded the kinetically favored 1:1 resin-bonded complex **2**.[10] Portions of **2** (0.02 g) were placed in 2-mL ampules and a given volume of *m*-xylene was injected directly into the polymer. The samples were sealed under a nitrogen atmosphere, allowed to equilibrate for 24 h at 25 °C, and then heated to 70 °C for 240 h. Infrared analyses of the resulting resins are summarized in Figure 1. Typical spectra obtained which reflect the amount of **2** and **3** present are shown in Figure 2. Addition of very small quantities of *m*-xylene (a good swelling solvent for **2**) resulted in a rapid increase in site–site interaction, i.e., formation of **3**. In the absence of solvent or in the presence of an excess of a poor swelling solvent such as *n*-hexadecane we observed no change in the IR spectrum from that of the starting 1:1 complex.[11,12] These results clearly establish that swelling is an important factor in site isolation in low cross-linked polystyrene resins.



The question of site isolation in highly cross-linked polystyrene is an important one and one which has not been fully answered. Grubbs et al. have presented compelling evidence that site isolation can be attained with a macroreticular 20% cross-linked polystyrene resin.[4] In contrast, Scott et al. have reported data which suggest that site–site interaction is significant in this same copolymer.[5] Unfortunately, in both studies a quantitative estimate of site–site interaction is not possible. Our observation that very little swelling was required for extensive site–site interaction in **2**, coupled with the fact that a good swelling solvent (methylene chloride) was used in

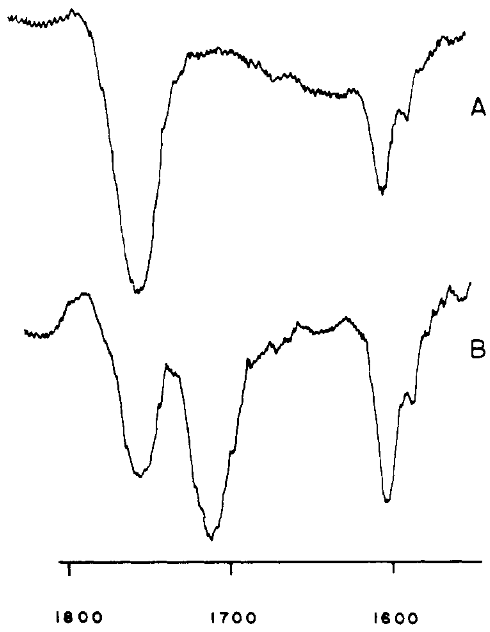


Figure 2. Typical infrared spectra (KBr) for **2** (A) and a mixture of **2** plus **3** (B).

Scott's study and a poor swelling solvent (cyclohexane) was employed by Grubbs, suggested to us that choice of solvent might also be an important factor in site isolation studies based on the macroreticular support. With this in mind, we have prepared a resin-bound complex analogous to **2**, using a 20% cross-linked macroreticular polystyryl–diphenylphosphine resin[13] and found that after heating for 168 h at 70 °C in the presence of an excess of *m*-xylene, only 35% of the cobalt remained as the 1:1 complex.[14] Similar experiments conducted with this same polymer in the absence of solvent or in the presence of excess *n*-hexadecane indicate no formation of the 2:1 complex. These results demonstrate that judicious choice of solvent is important for site isolation in high as well as low cross-linked polystyrene. We have also heated **2** for 168 h at 70 °C in the presence of an excess of *m*-xylene and found that approximately 38% remained unchanged. Although it is tempting to draw a quantitative comparison between **2** and the macroreticular resin for site isolation effectiveness, such a comparison is precluded by the uncertainty in the distribution of phosphine groups within each of the polymers.[15]

Acknowledgment. This manuscript was completed at the University of Georgia while S.L.R. was a Visiting Scientist. S.L.R. is grateful to the chemistry department for their kind hospitality.

References and Notes

(1) This work was supported by the National Science Foundation (Grant No. MPS74-23925) and the donors of the Petroleum Research Fund, administered by The American Chemical Society.

(2) S. L. Regen, *J. Am. Chem. Soc.*, **96**, 5275 (1974); S. L. Regen, *ibid.*, **97**, 3108 (1975); S. L. Regen, *Macromolecules*, **8**, 689 (1975); *J. Am. Chem. Soc.*, **99**, 3838 (1977).

(3) G. A. Crosby and M. Kato, *J. Am. Chem. Soc.*, **99**, 278 (1977).

(4) R. Grubbs, C. P. Lau, R. Cukier, and C. Brubaker, Jr., *J. Am. Chem. Soc.*, **99**, 4517 (1977); G. Gubitosa, M. Boldt, and H. H. Brintzinger, *ibid.*, **99**, 5174 (1977).

(5) L. T. Scott, J. Rebek, L. Ovsyanko, and C. L. Sims, *J. Am. Chem. Soc.*, **99**, 625 (1977).

(6) P. Jayalekshmy and S. Mazur, *J. Am. Chem. Soc.*, **98**, 6710 (1976).

(7) For a review which deals, in part, with site isolation on polystyrene resins, see J. I. Crowley and H. Rapoport, *Acc. Chem. Res.*, 135 (1976).

(8) J. P. Collman, L. S. Hegedus, M. P. Cooke, J. R. Norton, G. Dolcetti, and D. N. Marquardt, *J. Am. Chem. Soc.*, **94**, 1789 (1972).

(9) H. M. Relles and R. W. Schluenz, *J. Am. Chem. Soc.*, **96**, 6469 (1974); M. Farrall and J. M. J. Frechet, *J. Org. Chem.*, **41**, 3877 (1976).

(10) The disappearance of the $Co(NO)(CO)_3$ from the external liquid phase was measured by UV analysis. The resin-bonded complex was dried under vacuum (25 °C, 18 h, 0.05 mm) prior to IR analysis. The molar ratio of Co/P in the resin was 0.38.

(11) The degrees of swelling of **2** in *m*-xylene and *n*-hexadecane at 25 °C were 1.89 and 0.03 g of solvent/g of dry **2**, respectively.

(12) Crude kinetic measurements made for the reaction of 0.05 M $(C_6H_5)_3P$ with 0.01 M $Co(NO)(CO)_2[(C_6H_5)_3P]$ yielding $Co(NO)(CO)[C_6H_5)_3P]_2$ at 70 °C indicate the displacement to be approximately 2.0 times faster in *m*-xylene than in *n*-hexadecane.

(13) Polystyryl–diphenylphosphine (20% cross-linked) which contained 0.65 mmol of phosphine/g corresponding to 8% ring substitution was purchased from Strem Chemical Co. and was used as obtained. This material was prepared by direct lithiation of the copolymer with *n*-butyllithium/TMEDA followed by reaction with chlorodiphenylphosphine. The molar ratio of Co/P in the resulting resin was 0.30.

(14) The macroreticular form of polystyrene swells very little in all solvents. Due to voids located within this type of resin, the true degree of swelling cannot be obtained by weighing the swollen polymer. All site isolation studies with this support material were carried out with an excess of solvent.

(15) There presently is no method available for determining the distribution (molecular level) of pendant groups in functionalized cross-linked polystyrene.

(16) The NO band intensities were measured relative to a reference band in the polystyrene resin (1601 cm^{-1}); the molar intensity ratio ν_{NO}(1755 cm^{-1})/ν_{NO}(1710 cm^{-1}) was found to be 1.1. Results presented in Figure 1 correspond to the molar composition.

Steven L. Regen* and Dan P. Lee

Department of Chemistry, Marquette University
Milwaukee, Wisconsin 53233

Received August 8, 1977