Communications to the Editor

Degradation of Poly(α-methylstyrene) Initiated by Photoexcited Triphenylmethyl Cation

Recently the chemical behavior of photoexcited charged carbon species has received great attention. The studies on the highly stable triphenylmethyl cation (Ph_3C^+) have revealed that this entity is capable of undergoing a great variety of photoreactions, depending on the nature of solvent and the atmosphere.[1,2] In the absence of oxygen, it has been proposed by Cole et al. that the mechanistic scheme involves hydrogen abstraction from a suitable donor by the excited triphenylmethyl cation in the triplet state.[3,4]

In this paper we investigated the photochemical reactions of triphenylmethyl chloride (Ph_3CCl) in polar and nonpolar solvents in the presence of poly(α-methylstyrene) and studied the contribution of triphenylmethyl cation to the degradation of the polymer.

Poly(α-methylstyrene) (PMSt) was prepared by cationic polymerization at −78 °C and the number-average molecular weight of the polymer was 3.52×10^5. Ethylene dichloride (EDC) and benzene (Bz) were used as polar and nonpolar solvents, respectively.

Ph_3CCl was recrystallized twice from a benzene-light petroleum ether mixture in subdued light, mp 111–112 °C.

Figure 1 shows the absorption spectra of thoroughly degassed Ph_3CCl solutions containing PMSt. Similar spectra were obtained in the absence of the polymer. Although the concentration of Ph_3CCl was the same in both solutions (1.0×10^{-3} M), two significant differences were observed between the absorption spectrum in EDC and that in Bz. First, the absorption in Bz at wavelengths above 350 nm was greatly reduced, falling by a factor of 10 compared with that in EDC. Second, the spectrum in EDC showed two clear absorption maxima at 410 and 440 nm, whereas an almost structureless absorption was observed in Bz. The absorption spectrum in EDC is very similar to that of Ph_3C^+ obtained from the solution of triphenylcarbinol (Ph_3COH) in 99% sulfuric acid (curve 4 in Figure 1),[2] although the two absorption maxima were slightly shifted to the long-wave region and were opposite in intensity compared with the authentic spectrum. The spectrum in EDC agreed closely with that of Ph_3C^+ in methylene chloride reported by Subira et al.[5] so that the differences in the positions and relative intensity of the absorption maxima seem to be attributable to solvent environments.[6] The absorption in the 350–500-nm region in Bz was very small, which seems to indicate that the formation of Ph_3C^+ is difficult in the nonpolar solvent.[7] On adding a small amount of triethylamine (TEA) as a basic reagent to EDC solution, the absorption due to Ph_3C^+ disappeared completely as shown in Figure 1 (curve 3).[6]

Photoirradiations were carried out at 30 °C by the use of a 500-W high-pressure mercury lamp (Japan Storage Battery Co., Ltd.) and a Toshiba glass filter, UV-39, the transmission characteristic of which is shown in Figure 1. All the samples for irradiation were degassed by the several freeze–thaw cycles under high vacuum and then sealed off (ca. 1×10^{-5} mm of Hg).

Figure 2 shows the change in molecular weight of the polymer under various conditions, where M_0 is the initial number-average molecular weight, M_t is the molecular weight at irradiation time t, and the quantity ($M_0/M_t - 1$) is the average number of scissions per original polymer molecule. The determination of molecular weights was made on a gel-permeation chromatograph calibrated with PMSt standards in THF solution. Figure 2 demonstrates that the degradation of PMSt takes place rapidly in EDC solution, whereas no or slight degradation occurs in EDC solution containing TEA or in Bz solution. The polymer and solvents are transparent at wavelengths longer than 370 nm and no degradation was observed in the absence of Ph_3CCl for over 6 h of irradiation under vacuum. Moreover, no change in molecular weight was observed when the EDC solution containing PMSt and Ph_3CCl was allowed to stand in the dark for over 6 h. These results indicate that the photoexcited Ph_3C^+ is the chemically active species in the degradation of PMSt.

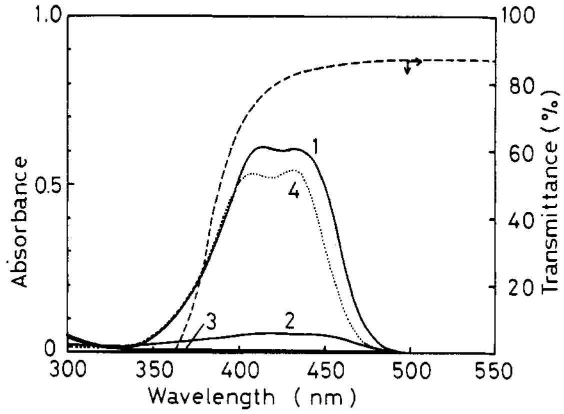

Figure 1. Absorption spectra of Ph_3CCl in various solvents: (1) in EDC, (2) in Bz, (3) TEA added in EDC, (4) in concentrated H_2SO_4 (ca. 10^{-5} M); (- - -) glass filter UV-39. [PMSt] = 2.1×10^{-2} M, [Ph_3CCl] = 1.0×10^{-3} M, [TEA] = 3×10^{-3} M. The optical path length = 1.0 cm.

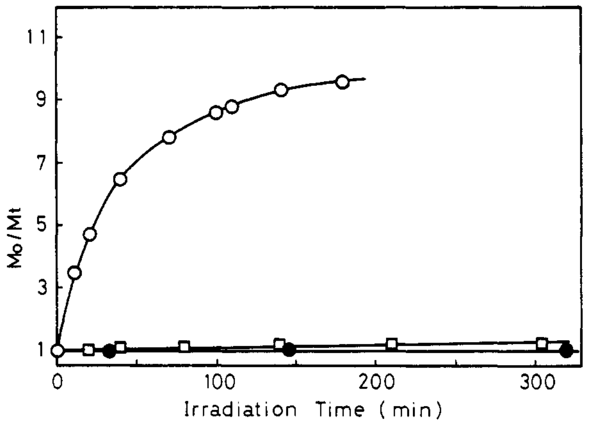

Figure 2. Photosensitized degradation of PMSt by Ph_3CCl under vacuum ($\lambda > 370$ nm): (○) in EDC, (□) in Bz, (●) TEA added in EDC. The concentrations of PMSt, Ph_3CCl, and TEA are the same as those in Figure 1.

Cole has reported that the primary process in the photoreactions of Ph_3C^+ is the abstraction of a hydrogen atom by the excited triplet cation.[3] Flash photolysis and spin-trapping techniques have proved that the scission of a C–C bond results from the abstraction of a hydrogen atom from methylene groups of PMSt main chain in the case of photosensitized degradation of PMSt by benzophenone.[8,9] Although the mechanism of the whole reaction still remains obscure, the degradation of PMSt in the present work seems to be initiated by the hydrogen abstraction from the polymer by the photoexcited Ph_3C^+.

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

$$\mathrm{PH} \xrightarrow{{}^3(\mathrm{Ph_3C^+})^*} \mathrm{P}\cdot \rightarrow \mathrm{P}_n\cdot + \mathrm{P}_m$$

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 $\mathrm{Ph_3CBr}$ and $\mathrm{Ph_3CS}_n\mathrm{Cl_5}$. They will be reported later.

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References and Notes

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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.

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 $\mathrm{Co(NO)(CO)_3}$.[8] Polystyryl–diphenylphosphine **1** was prepared from cross-linked polystyrene (Biobeads SX-2, 2% DVB, 200–400 mesh) by sequential bromination ($\mathrm{Br_2,BF_3}$), lithiation (n-BuLi, THF), and treatment with $\mathrm{(C_6H_5)_2PCl}$ 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 $\mathrm{Co(NO)(CO)_3}$ 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.

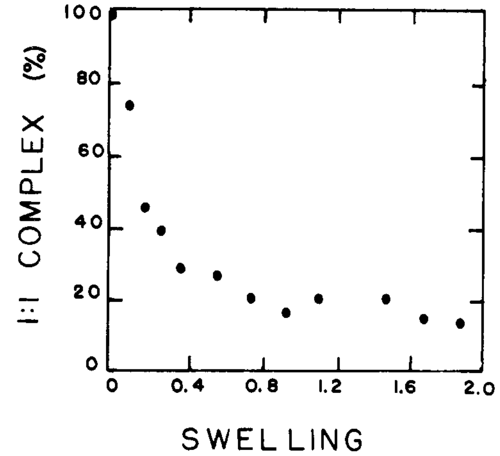
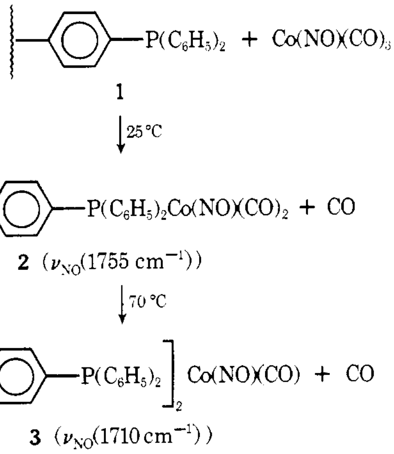


Figure 1. Plot of percent of 1:1 complex remaining as a function of degree of swelling, g of m-xylene/g of dry resin, of **2** after a reaction time of 240 h at 70 °C as estimated through relative IR band intensities.[16]



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