8226 *Macromolecules* **1997,** *30,* 8226−8232

Synthesis and Solid-State ^{13}C NMR Study of Polymer-Bound Triphenylmethyl Cations

Ting Tao and Gary E. Maciel*

Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523

Received July 8, 1997; Revised Manuscript Received October 23, 1997[⊗]

ABSTRACT: A polymer-bound cation system of the triphenylmethyl type has been synthesized via a method in which the first step is lithiation of polystyrene. The final step in the synthesis of the polystyrene-bound triphenylmethyl carbocation system was either conversion of the corresponding polymer-bound triphenylmethyl chloride with $AlCl_3$ or the conversion of the polymer-bound triphenylmethyl alcohol with perchloric acid. The various functionalized polymer samples were characterized by solid-state ^{13}C NMR, which showed that, for the polymer-bound triphenylmethyl alcohol system, there are 0.59 mmol of carbinol moieties per gram of polymer. The polymer-bound carbocation system was found to be surprisingly stable, even to moisture in air, and can readily be regenerated from its hydrolysis product. The polymer-bound carbocation system is effective as a catalyst in a Michael addition reaction and as a hydride acceptor reagent in a Dauben-type hydride transfer reaction.

Introduction

Anchoring a specific chemical functionality to a polymer such as polystyrene produces an insoluble reagent or catalyst, in which the functional groups are presumably randomly distributed and are accessible to reagents during subsequent reactions. This kind of technology is a rapidly growing field, involving applications in chemistry, industry, and biology, and there exist unlimited R&D possibilities by varying the polymer backbone and the functional groups bonded on the polymer. This kind of functionalized polymer is likely to be especially important in the future as environmentally friendly reagents or catalysts.[1] An example of a very toxic reagent that is easier to handle when immobilized on a polymer is HF adsorbed on poly(vinylpyridine), as described by Olah.[2]

The most common polymer-supported reagents or catalysts in synthetic chemistry are obtained by the chemical modification of unfunctionalized cross-linked polystyrene.[3] This is presumably because (i) the modifications are easily achieved by aromatic electrophilic or nucleophilic substitution, (ii) a hydrophobic surface is effective for adsorbing organic molecules, and (iii) the polymer is not degraded by moderately reactive chemical reagents under routine conditions. The use of functionalized, cross-linked polystyrene has proven to be successful in an enormous number of cases; examples include its remarkable use in the field of solid-phase organic synthesis, especially for peptides,[4] and its wide applicability in the form of commercial ion-exchange resins.[5] Indeed, great progress in the development of solid-phase synthetic methods is continually being made.[6]

The structural study of polymer-bound chemical agents by physicochemical techniques has lagged a long way behind their applications. Although infrared (IR) spectroscopy has shown its potential as an analytical technique to study supported reagents,[7] attempts to use IR for characterizing functionalized organic polymers can sometimes be frustrated by the fact that significant regions of the IR spectrum may be masked totally by absorptions due to the polymer backbone itself. Also, quantitation in IR spectroscopy can be problematic, and IR sample preparation techniques, such as the KBr-disk and self-supporting disk techniques, can lead to damage of the material. Ultraviolet−visible (UV−vis) spectroscopy has received little attention as a technique to study supported reagents, because of broad, often overlapping, bands in the UV−vis spectral region.[8] High-resolution solid-state ^{13}C NMR,[9] typically based on the techniques of magic-angle spinning (MAS) and high-power proton decoupling[10] and often combined with cross polarization (CP),[11] has recently figured prominently among the host of investigative methods used in the study of polymer systems.[12] Such techniques offer the prospect of studying the local environments and active sites of polymer-bound functionalities, which should improve the fundamental understanding of the mode in which a polymer-bound reagent functions and perhaps how it can be improved. This prospect is especially attractive in light of the importance and popularity of combinatorial chemistry strategies.[13]

In spite of its success in characterizing surface species on inorganic supports (e.g., oxides),[14] solid-state NMR techniques are as yet somewhat less popular for studying the behaviors of functionalities of reagents on organic supports. There are a few cases[15] involving studies of phosphorus-containing and aluminum-containing functionalities on organic polymers by using ^{31}P and ^{27}Al NMR; these studies have taken advantage of the high NMR sensitivities of ^{31}P and ^{27}Al nuclei. In many cases it might be most useful to study ^{13}C nuclei within the polymer-bound functionality, because the most crucial element in organic functionalities is typically carbon. Unfortunately, ^{13}C signals from the polymer framework will in some cases conceal the ^{13}C NMR information embodied in dilute functionalities. Therefore, it would appear that ^{13}C-enriched samples may often be required for the study of specific organic functionalities bound to organic polymers. Shea and Sasaki[16] showed that ^{13}C CP-MAS NMR can be an extraordinarily valuable technique in providing molecular-level details of binding interactions in a functionalized polymer, which in their case was prepared by a molecular imprinting[17] method.

The triphenylmethyl cation, $(C_6H_5)_3C^+$, in solution plays a substantial role in synthetic chemistry as a catalyst[18] and as a hydride abstraction reagent.[19] In contrast, a polymer-bound triphenylmethyl cation has

---

[⊗] Abstract published in *Advance ACS Abstracts,* December 15, 1997.

S0024-9297(97)01004-8 CCC: $14.00

apparently only once been reported in organic synthesis, as a catalyst in cross aldol condensation reactions,[20] and has never been characterized by spectroscopic techniques. However, information from spectroscopic probes is necessary for understanding the detailed identities of the polymer-attached chemical functionalities and for the design of second-generation polymer-supported reagents with enhanced catalytic activity. In a continuation of our interest in carbocations of the $(C_6H_5)_3C^+$ type,[21] the synthesis of polystyrene-attached ^{13}C-labeled triphenylmethyl carbenium ion, its characterization by solid-state NMR techniques, and its diagnostic chemical behavior are presented and discussed in this paper.

Experimental Section

Materials. Polystyrene-1% divinylbenzene copolymer beads, **1** (100−200 mesh), were obtained from Acros Organics, Pittsburgh, PA. ^{13}C-labeled benzoic acid (99% ^{13}C-carboxyl) was purchased from Cambridge Isotopes Laboratory. Cyclohexane (from Aldrich) and dichloromethane (from J. T. Baker Chemical Co.) were first dried over 4 Å molecular sieves for 24 h and then refluxed over calcium hydride for another 24 h. Benzene (from J. T. Baker) was first dried over 4 Å molecular sieves for 24 h and then refluxed over sodium for another 24 h. Tetrahydrofuran (from Fisher Scientific Co.) was pre-dried over calcium chloride, and then refluxed over sodium pieces and benzophenone for 24 h. Thionyl chloride (from Fisher Scientific Co.) was used immediately after distillation. All other chemicals were purchased from Aldrich and used as received.

Synthesis of ^{13}C-Labeled Benzophenone (3). ***Step 1.***[22] A 3.00 g sample of ^{13}C-labeled benzoic acid (99% ^{13}C-carboxyl) and 3.65 g of redistilled thionyl chloride in a 15 mL flask were heated on a boiling water bath (~95 °C) until the evolution of hydrogen chloride ceased (about 3 h). After the flask was cooled, the condenser was detached and a distillation head was fitted to the flask. In the subsequent distillation, ^{13}C-labeled benzoyl chloride was collected at 189−194 °C (745 Torr). The yield was 3.08 g (80%) of clear, colorless liquid. ***Step 2.*** The benzoyl chloride product (3.02 g) from the previous step was added slowly into a stirred mixture of 15 mL of sodium-dried benzene and 3.50 g of anhydrous aluminum trichloride in a 50 mL flask. The reaction was completed by heating on a water bath at 50 °C until HCl was no longer evolved. The contents of the flask were cooled in an ice bath to 0 °C, and a mixture of 25 mL of cold water and 10 mL of concentrated HCl was added. The organic layer was separated and washed with 5% aqueous NaOH and then with water and dried with anhydrous magnesium sulfate. After removal of benzene by a rotary evaporator, the residue was recrystallized from petroleum ether, and 2.78 g (72%) of ^{13}C-labeled benzophenone (**3**) was collected: mp 45−47 °C. ^{13}C NMR ($CDCl_3$): 196.8 ppm (^{13}C- label). ^{1} H NMR ($CDCl_3$), δ: 7.81−7.77 (m, 4H), 7.61− 7.55 (m, 2H), 7.50−7.44 (m, 4H).

Synthesis of Polymer-Bound ^{13}C-Labeled Triphenylmethanol (4). ***Step 1.*** A 5.0 g sample of polystyrene−1% divinylbenzene copolymer (**1**) was suspended in 50 mL of CaH_2-dried cyclohexane under N_2(g). To this mixture was added 10 mL of *n*-butyllithium (10 mmol, 1.0 M in cyclohexane), followed by 1.5 mL of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) (10 mmol), by a syringe. The slurry was heated to 60 °C in an oil bath and stirring continued at this temperature for 12 h. The resulting lithiated polymer (**2**) was filtered under N_2(g), washed with three 50 mL portions of dried cyclohexane, and used immediately for the next reaction step. ***Step 2.*** To a suspension of polymer **2** (from step 1) in 50 mL of dried cyclohexane under nitrogen protection was added a total of 1.0 g of 99% ^{13}C-labeled benzophenone, **3** (or a 1:1 mixture of ^{13}C-labeled and natural-abundance benzophenone), in 10 mL of dry cyclohexane, in small portions over a 1 h period at room temperature. The mixture was stirred for three additional hours in a 60 °C oil bath. The mixture was then treated with 25 mL of a 1:1 (vol:vol) THF−water solution and filtered, washed with three 20 mL portions of water, three 20 mL portions of ethanol, and three 20 mL portions of diethyl ether, and then dried under vacuum (10^{-2} Torr) at room temperature for about 12 h. A 5.8 g yield of polymer-bound ^{13}C-labeled triphenylmethanol (**4**), a white powder, was obtained.

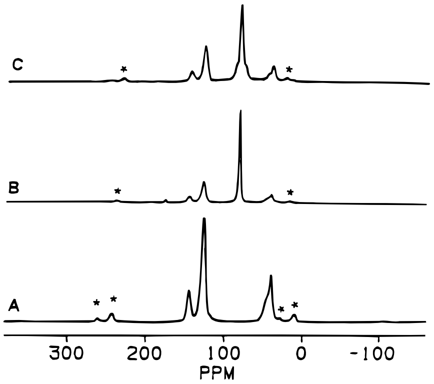


Figure 1. ^{13}C CP-MAS spectra of polymer-bound materials (peaks marked with asterisks correspond to spinning sidebands): ^{1}H 90° pulse, 5.7 μs; CP contact time, 2 ms; ^{1}H decoupling, 43 kHz. Key: (A) polystyrene (**1**), obtained with a 2 s repetition delay and 20 000 scans; (B) polymer-bound triphenylmethanol (**4**), obtained with a 5 s repetition delay and 1000 scans; (C) polymer-bound triphenylmethyl chloride (**5**), obtained with a 5 s repetition delay and 1000 scans.

Synthesis of Polymer-Bound ^{13}C-Labeled Triphenylmethyl Chloride (5). A mixture of 1.0 g of polymer **4**, 10 mL of dried tetrahydrofuran and 1.0 mL of redistilled thionyl chloride was stirred at 60 °C in an oil bath for 10 h under N_2(g) protection. The polymer was rapidly filtered, washed with two 25 mL portions of sodium-dried benzene, and dried under vacuum (10^{-2} Torr) at room temperature for about 12 h. A 1.0 g yield of polymer-bound ^{13}C-labeled triphenylmethyl chloride (**5**), a white powder, was obtained.

Synthesis of Polymer-Bound ^{13}C-Labeled Triphenylmethylium Tetrachloroaluminate (6a). To a suspension of 0.45 g of polymer **5** in 10 mL of dried cyclohexane was added 0.15 g of $AlCl_3$(s), and the mixture was stirred for 10 h under N_2(g) at room temperature. After removal of cyclohexane at 25 °C under vacuum (10^{-3} Torr), 0.58 g of polymer-bound ^{13}C-labeled triphenylmethylium tetrachloroaluminate (**6a**), a purple powder, was collected.

Synthesis of Polymer-Bound ^{13}C-Labeled Triphenylmethylium Perchlorate (6b). A mixture of 1.0 g of polymer-bound triphenylmethanol (**4**) with 0.30 mL of 70% $HClO_4$ and 8.0 mL of acetic anhydride was stirred at room temperature under N_2(g) for 5 h. The resulting purple reaction mixture was filtered under N_2(g). The resulting solid residue was dried at room temperature under vacuum (10^{-3} Torr), and 1.0 g of polymer-bound ^{13}C-labeled triphenylmethylium perchlorate (**6b**), a purple powder, was obtained.

The FT-IR (DR) and solid-state ^{13}C NMR spectra of all the polymer-bound samples, **4, 5, 6a,** and **6b,** are shown in Figures 1−3.

Synthesis of 1,3,5-Triphenyl-1,5-Pentanedione (7). A mixture of 0.050 g of the polymer **6b** (0.029 mmol triphenylmethyl cation), 0.091 g of *trans*-1,3-diphenyl-2-propen-1-one, $C_6H_5CH{=}CHCOC_6H_5$ (0.43 mmol), and 0.12 g of 1-phenyl-1-(trimethylsiyloxy)ethylene, $CH_2{=}C(C_6H_5)OSi(CH_3)_3$ (0.62 mmol), in dry dichloromethane (4.0 mL), was stirred at −78 °C under dry N_2(g) protection. After the reaction was complete (about 30 min, checked by thin layer chromatography), the polymer-bound catalyst **6b** was separated from the organic layer by filtration. Then, the organic layer was washed with 3.0 mL of 10% aqueous $NaHCO_3$ and dried over anhydrous Na_2SO_4. Finally, the solvent was removed with a rotary evaporator, and the residue was separated by silica gel column chromatography, using a 1:10 (vol:vol) ethyl acetate−hexane solution as eluting solvent. The product, 1,3,5-triphenyl-1,5-pentanedione, was obtained in 86% yield (0.12 g, 0.37 mmol), mp 80.5−81.5 °C. ^{1}H NMR ($CDCl_3$), δ (ppm): 7.95 (d, 4H), 7.55 (t, 2H), 7.44 (t,4H), 7.28−7.18 (m, 5H), 4.07 (quintet, 1H),

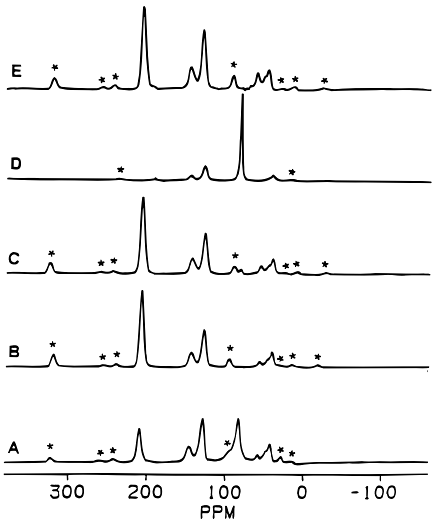


Figure 2. ^{13}C CP-MAS spectra of polymer-bound materials (peaks marked with asterisks correspond to spinning sidebands): ^{1}H 90° pulse, 5.7 μs; CP contact time, 2 ms; ^{1}H decoupling, 43 kHz; 5 s repetition delay and 1000 scans. Key: (A) product of reaction of polymer **5** with $AlCl_3$ (**6a**); (B) product of reaction of polymer **4** with $HClO_4$ (**6b**); (C) sample **6b** exposed to 80% humidity for 1 day; (D) product of reaction of polymer **6b** with 50/50 (vol/vol) THF/H_2O; (E) product of reaction of the polymer of Figure 2D with $HClO_4$.

3.49 (d, d, 2H), 3.36 (d, d, 2H). ^{13}C NMR ($CDCl_3$), δ (ppm): 37.1, 44.9, 126.7, 127.4, 128.1, 128.5, 128.6, 133.1, 136.8, 143.8, 198.6.

Synthesis of Cycloheptatrienylium (Tropylium) Perchlorate (8). To a mixture of 0.25 g of polymer **6b** and 4.0 mL of acetonitrile was added 15 mg of cycloheptatriene (Aldrich) dropwise by a syringe at room temperature under a $N_2(g)$ atmosphere. The resulting mixture was stirred under dry $N_2(g)$ protection for 20 min. The organic layer was separated from the polymer by filtration, and the acetonitrile was removed at 25 °C under vacuum (10^{-3} Torr). A 32 mg (98%) yield of cycloheptatrienylium perchlorate, a light brown solid, was obtained, mp 92.0−93.5 °C. ^{1}H NMR (CD_3CN), δ (ppm): 7.56. ^{13}C NMR (CD_3CN), δ (ppm): 156.3.

Spectroscopy. All ^{13}C MAS NMR spectra shown were obtained at 22.71 MHz on a Chemagnetics M-90s spectrometer. Kel-F rotors were used at a spinning speed of about 2.5 kHz. For cross polarization (CP) experiments: ^{1}H 90° pulse, 5.7 μs; CP contact time, 2 ms; repetition time, 2−5 s; ^{1}H decoupling, 43 kHz. For direct polarization (DP) experiments (no cross polarization): a ^{13}C 90° pulse of 5.5 μs, with 50 kHz ^{1}H decoupling; repetition time, 200 s. ^{1}H and ^{13}C liquid-solution NMR spectra were recorded on a Bruker AC 300 FT NMR spectrometer. IR spectra were taken on a Perkin-Elmer 1600 Series FTIR spectrometer, using a diffuse reflectance (DR) adapter.

Results and Discussion

As shown in Scheme 1, direct lithiation of cross-linked polystyrene (**1**) was achieved using *n*-butyllithium and tetramethylethylenediamine (TMEDA) in cyclohexane, as reported previously.[23] The lithiated polystyrene (**2**) produced was subsequently reacted with ^{13}C-labeled benzophenone (**3**) to give polymer-bound triphenylmethanol (**4**). The benzophenone was carbonyl-^{13}C-labeled at 99% (in some experiments, 50%) for ease of ^{13}C NMR detection in the presence of background signals from the polymer network. The resulting polymer-immobilized triphenylmethanol was converted to the carbocation product (**6**) either by direct reaction with perchloric acid (pathway **a**), or by Lewis acid-base reaction with $AlCl_3$ via the polymer-bound triphenylmethyl chloride (**5**), prepared with thionyl chloride (pathway **b**).

Scheme 1. Preparation of the Polymer-Bound Triphenylmethyl Cation from Polystyrene

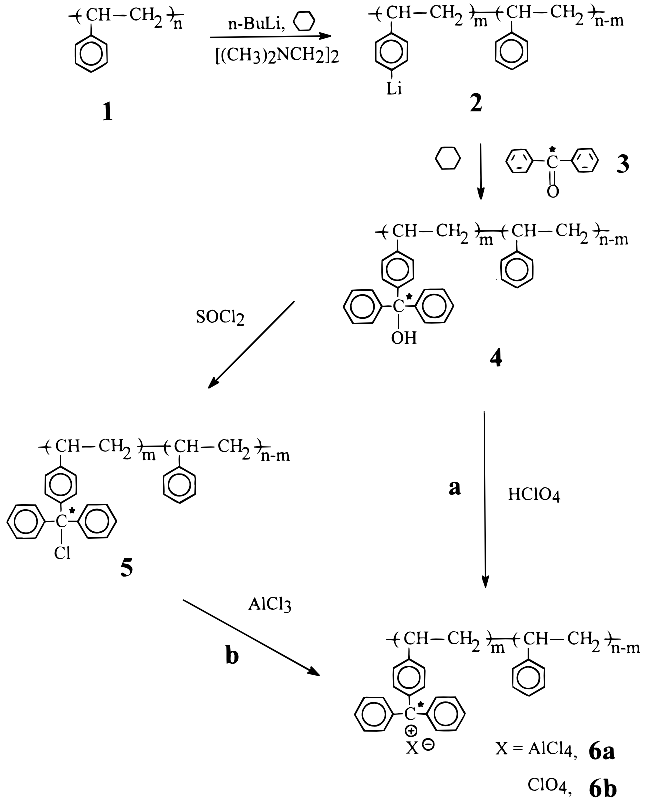


Figure 1A shows the ^{13}C CP-MAS spectrum of the unaltered polystyrene (**1**), showing the expected peaks due to aromatic and aliphatic carbons. After lithiation of polystyrene−1% divinylbenzene copolymer **1** and subsequent reaction with ^{13}C-labeled benzophenone **3**, the resulting modified polymer **4** shows a major ^{13}C NMR peak at 82 ppm (Figure 1B), which confirms the presence of the triphenylmethanol functionality. The corresponding chloride derivative **5,** prepared by refluxing polymer **4** with thionyl chloride in dry tetrahydrofuran, yields the spectrum of Figure 1C, which is very similar to that of polymer **4,** except for some broadening of the peak at 82 ppm. This broadening might result from incomplete MAS averaging of dipolar interactions due to the proximity to quadrupolar chlorine nuclei. The ^{13}C chemical shifts of triphenylmethanol and triphenylmethyl chloride are both about 82 ppm.[24] The IR spectrum shows a strong O−H stretch absorption at 3560 cm^{-1} for polymer **4** (Figure 3A), while no absorption in that region is seen for polymer **5** (Figure 3B).

Preparation of the sample corresponding to Figure 2A was based on analogy to our previous report [21] that reaction of the Lewis acid $AlCl_3$ with the Lewis base $(C_6H_5)_3{}^{13}CCl$ yielded the triphenylmethyl cation. Indeed, the reaction between $AlCl_3$ and P-$(C_6H_4)^{13}C(C_6H_5)_2$-Cl (where P represents the polymer framework) in dry cyclohexane to form P-$(C_6H_4)^{13}C^+(C_6H_5)_2$ (**6a**) is at least partially successful, as shown in Figure 2A, where there is a substantial P-$(C_6H_4)^{13}C^+(C_6H_5)_2$ peak at 209 ppm. Unfortunately, this reaction did not proceed to completion, as evidenced by the remaining carbocation-precursor signal (82 ppm) in Figure 2A. This situation may result simply from a lack of intimate, efficient access of the polymer's cation-precursor sites by the essential $AlCl_3$ species, especially for interior active sites of the polymer. Such interior active sites may be in less mobile regions of the polymer network, reducing the

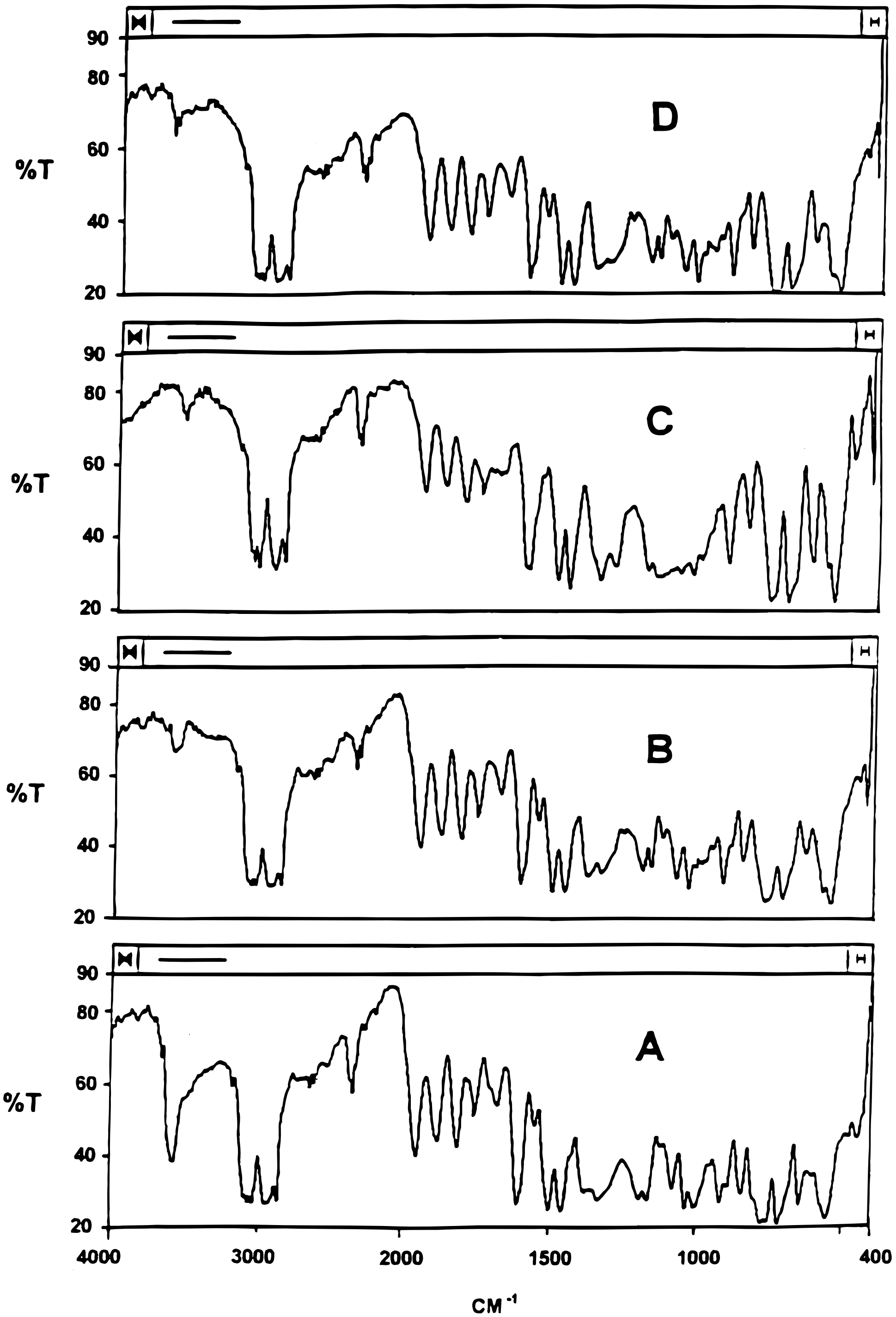


Figure 3. FT-IR (diffuse reflectance) spectra: (A) polymer-bound triphenylmethanol (**4**); (B) polymer-bound triphenylmethyl chloride (**5**); (C) polymer-bound triphenylmethyl cation (**6a**); (D) polymer-bound triphenylmethyl cation (**6b**).

accessibility to $P\text{-}(C_6H_4)^{13}C(C_6H_5)_2Cl$ sites by $AlCl_3$ species. It has been reported that the mobility of species bound to polymer chains and the motion of reactants located within their solvent-swollen pores are directly related to the degree of swelling of a solvent.[25] Providing a more efficient pathway for the direct transformation of polymer **4** to polymer **6b,** perchloric acid was found to be an excellent Brönsted acid reagent for producing the polymer bound carbocation (Figure 2B) via pathway **a** in Scheme 1; the only ^{13}C signal in Figure 2B that is not present in the spectrum (Figure 1A) of the unaltered polystyrene (i.e., arising from ^{13}C labeling) is that of $P\text{-}(C_6H_4)^{13}C^+(C_6H_5)_2$ at 209 ppm; i.e., the polymer-bound alcohol functionality can all be converted by $HClO_4$ to the corresponding carbocation form.

The polymer-bound triphenylmethyl carbenium perchlorate (**6b**) is very stable when stored at room temperature under a dry $N_2(g)$ atmosphere; the spectrum taken from a sample that was stored in a MAS rotor in a $N_2(g)$ glovebox for 1 month at room temperature is almost identical to the spectrum of Figure 2B. More surprisingly, even when sample **6b** was exposed to 80% humidity (in a closed humidifier containing saturated NH_4Cl aqueous solution at 25 °C) for 24 h, the carbenium ion sites were still stable on the polymer, as shown in Figure 2C. When sample **6b** was stirred at room temperature with THF/H_2O (50/50 vol) for 4 h, washed with ethanol and diethyl ether and dried at 25 °C under vacuum (10^{-2} Torr), the cation was converted back to triphenylmethyl alcohol; the ^{13}C CP-MAS spectrum

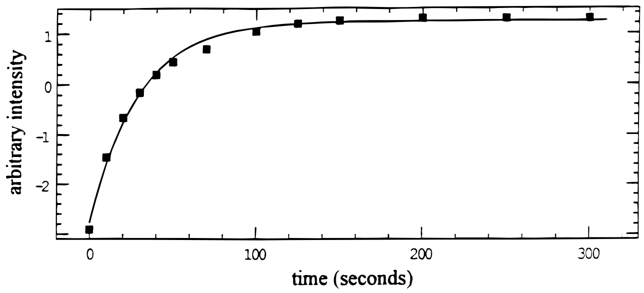


Figure 4. ^{13}C T_1 data analysis for sample **4**. The experimental data are shown with the symbol ■. The curve was obtained from a least-squares fit of the experimental intensity data (integrated) to eq 1.

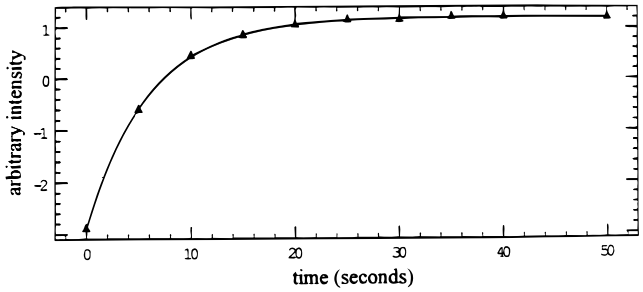


Figure 5. ^{13}C T_1 data analysis for [^{13}C-carboxyl]glycine. The experimental data are shown with the symbol ▲. The curve was obtained from a least-squares fit of the experimental intensity data (integrated) to eq 1.

(Figure 2D) from the hydrolyzed polymer shows that the 209 ppm peak is missing and the 82 ppm peak has reappeared. By treating the hydrolysis sample shown in Figure 2D with $HClO_4$, the polymer-bound triphenylmethylium functionality can be regenerated, as evidenced by the spectrum in Figure 2E.

^{13}C spin counting experiments on the amount of polymer-bound triphenylmethanol functionality in sample **4** were carried out in order to determine the loading level of the immobilized functionality on the polymer. For implementation of this quantitative analysis, the ^{13}C CP-MAS inversion−recovery method [26] was used to measure the ^{13}C spin−lattice relaxation times, $T_1{}^{C}$, of sample **4** and a reference compound, [^{13}C-carboxyl]-glycine. In plots of the signal intensity *vs.* the delay τ between the two pulses in the inversion−recovery sequence, a single exponential fit was displayed for each of the two compounds, according to eq 1. In this

$$M(\tau) = [M_{\mathrm{CP}}(0) - M_0]\exp(-\tau/T_1{}^{\mathrm{C}}) + M_0 \qquad (1)$$

equation, M(τ) is the longitudinal ^{13}C magnetization corresponding to the ^{13}C signal intensity for a given delay τ, $M_{\mathrm{CP}}(0)$ is its initial value, M_0 is its equilibrium value, and $T_1{}^{C}$ is the ^{13}C spin−lattice relaxation time. The computer fit yields a $T_1{}^{C}$ value for the labeled carbon in sample **4** of 29 s (Figure 4), and for an intensity reference compound ([^{13}C-carboxyl]glycine) a value of 6.1 s was obtained (Figure 5). Then, from the intensity ratio obtained in a ^{13}C DP-MAS experiment (direct polarization, no CP) carried out with a 200 s repetition delay (~7 × $T_1{}^{C}$ of sample **4**) on a mixture of **4** (0.8626 g) and glycine (0.0709 g) (Figure 6), it was readily determined that the loading level of the bound triphenylmethanol on the polymer is 0.59 mmol/g of polymer. This corresponds to $(n - m)/m = 13$ in Scheme 1.

To begin exploring the synthetic utility of the polymer-bound triphenylmethyl carbocation **6b**, we employed it in the 50% ^{13}C-labeled form as a *catalyst* in the Michael addition reaction shown in eq 2.

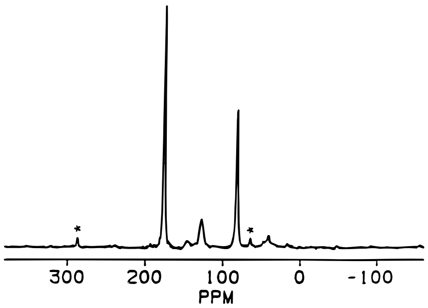
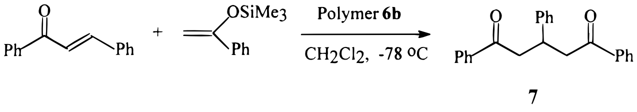


Figure 6. ^{13}C DP-MAS spectrum of a mixture of polymer **4** (0.8626 g) and [^{13}C-carboxyl]glycine (0.0709 g), obtained with a 90° pulse of 5.5 μs, 50 kHz ^{1}H decoupling, a repetition delay of 200 s, and 96 scans.

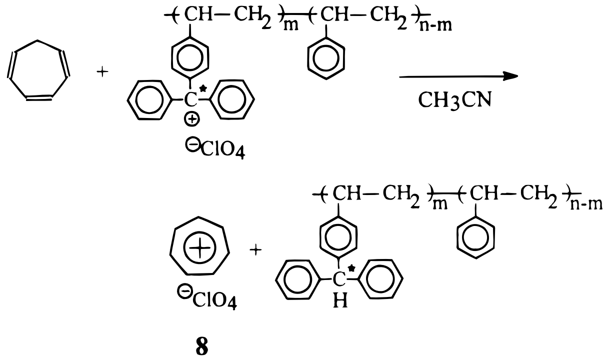


(2)

The Michael adduct, 1,3,5-triphenyl-1,5-pentanedione (**7**), was obtained in good yield (86%) by the reaction of the silyl enol ether of acetophenone with an α,β-unsaturated ketone (1,3-diphenyl-2-propen-1-one, or *trans*-chalcone) in the presence of polymer **6b**. The same overall reaction has been carried out by Kobayashi *et al.*[18a] with a 92% yield by using triphenylmethylium perchlorate as a catalyst *in solution*.

Compared to the conventional route using solid inorganic Lewis acids (e.g., $TiCl_4$)[27] or trityl perchlorate in solution[18] as catalysts in aldol and Michael reactions, the advantage of this polymer-immobilized catalyst is its potential for ready recoverability and hence its potential as an environmentally friendly alternative to corrosive, toxic, and wasteful reagents. However, ^{13}C CP-MAS spectra taken before (Figure 7A) and after (Figure 7B) catalysis of the Michael addition reaction show that the polymer-supported triphenylmethyl cation catalyst (peak at 209 ppm) was partially deactivated by hydrolysis (peak at 82 ppm) and hydride abstraction (peak at 57 ppm). The hydrolyzed sites might be easily regenerated by repeating pathway **a** in Scheme 1, while hydride-poisoned sites remain a challenge for recycling, for which one would have to find a suitable oxidation pathway to convert P-$(C_6H_4)^{13}CH(C_6H_5)_2$ back to P-$(C_6H_4)^{13}C^+(C_6H_5)_2$.

The functionalized polymer **6b** was also examined as a hydride abstraction *reagent* in a Dauben-type hydride-transfer reaction,[19(a)] i.e., hydride transfer from cycloheptatriene to the polymer-attached carbocation (eq 3).



(3)

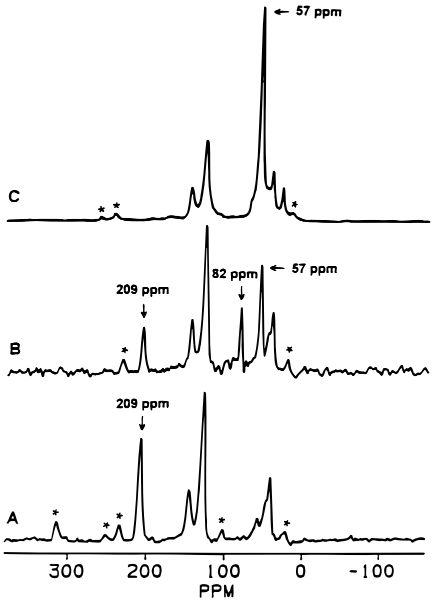


Figure 7. ^{13}C CP-MAS spectra of 50% ^{13}C-labeled polymer-bound triphenylmethyl cation (**6b**) (^{1}H 90° pulse, 5.7 μs; CP contact time, 2 ms; ^{1}H decoupling, 43 kHz; 5 s repetition delay; 1000 scans): (A) before functioning as a catalyst; (B) after functioning as a catalyst in the Michael addition reaction (eq 2); (C) after acting as a hydride abstraction reagent in the Dauben reaction (eq 3).

The method is successful, with nearly quantitative yield (98%) of tropylium perchlorate (**8**), which is easily separated from the polymer-bound reagent and product. The ^{13}C CP-MAS spectrum of the polymer reagent after hydride transfer reaction shows that all carbocations were converted to polymer-bound triphenylmethane (peak at 57 ppm), i.e., P-$(C_6H_4)^{13}CH(C_6H_5)_2$, as shown in Figure 7C. The corresponding process carried out using triphenylmethylium tetrafluoroborate in solution provided a 90% yield.[19d]

Conclusions

The present work has shown directly that a functionalized, cross-linked polymer with attached carbenium ions of the triphenylmethyl type can be synthesized efficiently by the chemical modification of polystyrene and that the polymer-immobilized (bound) carbocation is quite stable, compared to the analogous carbocation formed on (in) zeolite HY, as described previously.[21]

Solid-state ^{13}C NMR techniques provide a very direct approach for characterizing a polymer-supported reagent, and its entire preparation process. Although IR might be an alternative tool, the limitation of its application in this field is quite obvious due to overlapping signals from the polymer backbone. For example, IR spectra shown in parts B–D of Figure 3 provide little information for distinguishing polymers **5**, **6a**, and **6b**, while NMR can readily tell the difference between these differently functionalized polymers.

The polymer-bound triphenylmethyl carbenium system was found to be effective in catalyzing the Michael addition reaction of an α,β-unsaturated ketone with a silyl enol ether, and as a hydride abstraction reagent in converting cycloheptatriene to tropylium cation. This kind of polymer-bound carbocation might have further potential implications in chemical research as a reagent in solid phase synthesis, and in industry as a catalyst in continuous-flow processes.[28] Also, this polymer-attachment method could provide a useful strategy for studying a variety of carbocations or other reactive species in solid phases.

Acknowledgment. The authors gratefully acknowledge partial support of this research by the BP America Research Foundation.

References and Notes

(1) (a) Itsuno, S. In *Polymeric Materials Encyclopedia; Synthesis, Properties, and Applications*; Salamone, J. C., Ed.; CRC Press: Boca Raton, FL, 1996; p 8078. (b) Alexandratos, S. D.; Crick, D. W. *Ind. Eng. Chem. Res.* **1996**, *35*, 635. (c) Pittman Jr., C. U. *Polym. News* **1995**, *20*, 182. (d) Fréchet, J. M. J.; Darling,G. D.; Itsuno, S.; Lu, P. Z.; V de Meftahi, M.; Rolls Jr. W. A. *Pure Appl. Chem.* **1988**, *60*, 353.

(2) Olah, G. A.; Li, X.; Wang, Q.; Prakash, G. K. S. *Synthesis* **1993**, 693.

(3) (a) Spitzer, J. L.; Kurth, M. J.; Schore, N. E.; Najdi, S. D. *Tetrahedron* **1997**, *53*, 6791. (b) Itsuno, S.; Sakurai, Y.; Ito, K.; Maruyama, T.; Nakahama, S.; Fréchet, J. M. J. *J. Org. Chem.* **1990**, *55*, 304. (c) Deratani, A.; Darling, G. D.; Horak, D.; Fréchet, J. M. J. *Macromolecules* **1987**, *20*, 767. (d) Darling, G. D.; Fréchet, J. M. J. *J. Org. Chem.* **1986**, *51*, 2270. (e) Akelah, A.; Sherrington, D. C. *Chem. Rev.* **1981,** *81*, 557. (f) Molinari, H.; Montanari, F.; Quici, S.; Tundo, P. *J. Am. Chem. Soc.* **1979**, *101*, 3920. (g) Harrison, C. R.; Hodge, P. *J. Chem. Soc., Perkin Trans. 1*, **1976**, 605. (h) Relles, H. M.; Schluenz, R. W. *J. Am. Chem. Soc.* **1974**, *96*, 6469. (i) Collman, J. P.; Hegedus, L. S.; Cooke, M. P.; Norton, J. R.; Dolcetti, G.; Marquardt, D. N. *J. Am. Chem. Soc.* **1972**, *94*, 1789.

(4) (a) Merrifield, R. B. *Angew. Chem., Int. Ed. Engl.* **1985,** *24*, 799. (b) Merrifield, R. B. *J. Am. Chem. Soc.* **1963**, *85*, 2149.

(5) Maud, J. M. In *Solid Supports and Catalysts in Organic Synthesis*; Smith, K., Ed.; Ellis Horwood: New York, 1992; p 58.

(6) (a) Stranix, B. R.; Liu, H. Q.; Darling, G. D. *J. Org. Chem.* **1997**, *62*, 6183. (b) Morphy, J. R.; Rankovic, Z.; Rees, D. C. *Tetrahedron Lett.* **1996**, *37*, 3209. (c) Jung, G.; Fruchtel, J. S. *Angew. Chem.* **1996**, *35*, 17. (d) Sheppard, R. C. *Trends Biotechnol.* **1993**, *11*, 492.

(7) Henniker, J. C. *Infra-red Spectrometry of Industrial Polymers*; Academic Press: New York, 1967.

(8) Clark, J. H.; Kybett, A. P.; Macquarrie, D. J. *Supported Reagents: Preparation, Analysis, and Applications;* VCH Publishers: New York, 1992; p 86.

(9) Maciel, G. E. *Science* **1984**, *226*, 282.

(10) Schaefer, J.; Stejskal, E. O. *J. Am. Chem. Soc.* **1976**, *98*, 1031.

(11) Pines, A.; Gibby, M. G.; Waugh, J. S. *J. Chem. Phys.* **1973**, *59*, 569.

(12) McBrierty, V. J.; Packer, K. J. *Nuclear Magnetic Resonance in Solid Polymers;* Cambridge University Press: New York, 1993.

(13) (a) Szostak, J. W. *Chem. Rev.* **1997**, *97*, 347. (b) Shapiro, M. J.; Chin, J.; Jarosinski, M. A. *Tetrahedron Lett.* **1997**, *38*, 1333.

(14) (a) Hays, G. R.; Clague, A. D. H.; Huis, R.; Van der Velder, G. *Appl. Surf. Sci.* **1982**, *10*, 247. (b) Caravajal, G. S.; Leyden, D. E.; Quinting, G. R.; Maciel, G. E. *Anal. Chem.* **1988**, *60*, 1776.

(15) (a) Maciel, G. E.; O'Donnell, D. J.; Greaves, R. In *Catalytic Aspects of Metal Phosphine Complex*, Alyea, E. C.; Meek, D. W. Ed.; Advances in Chemistry 196; American Chemical Society: Washington, DC, 1982; p 389. (b) Renaud, E.; Baird, M. C. *J. Mol. Catal.* **1993**, *80*, 43. (c) Chung, T. C. In *Polymeric Materials Encyclopedia,; Synthesis, Properties, and Applications*; Salamone, J. C., Ed.; CRC Press: Boca Raton, FL, 1996; p 8093.

(16) Shea, K. J.; Sasaki, D. Y. *J. Am. Chem. Soc.* **1991**, *113*, 4109.

(17) Wulff, G. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1812.

(18) (a) Kobayashi, S.; Matsui, S.; Mukaiyama, T. *Chem. Lett.* **1988**, 1491. (b) Mukaiyama, T.; Leon, P.; Kobayashi, S. *Chem. Lett.* **1988**, 1495. (c) Mukaiyama, T.; Kobayashi, S.; Shoda, S. *Chem. Lett.* **1984**, 907. (d) Mukaiyama, T.; Kobayashi, S.; Murakami, M. *Chem. Lett.* **1984**, 1759. (e) Kobayashi, S.; Murakami, M.; Mukaiyama, T. *Chem. Lett.* **1985**, 953.

(19) (a) Dauben Jr., H. J.; Gadecki, F. A.; Harmon, K. M.; Pearson, D. L. *J. Am. Chem. Soc.* **1957**, *79*, 4557. (b) Patton, A. T.; Strouse, C. E.; Knobler, C. B.; Gladysz, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 5804. (c) Bodner, G. S.; Gladysz, J. A.; Nielsen,

M. F.; Parker, V. D. *J. Am. Chem. Soc.* **1987**, *107*, 1757. (d) Dauben Jr., H. J.; Honnen, L. R.; Harmon, K. M. *J. Org. Chem.* **1960**, *25*, 1442.
(20) Mukaiyama, T.; Iwakiri, M. *Chem. Lett.* **1985**, 1363.
(21) (a) Tao, T.; Maciel, G. E. *J. Am. Chem. Soc.* **1995**, *117*, 12889. (b) Tao, T. Ph.D. Dissertation, Colorado State University, 1997.
(22) Vogel, A. I. *Textbook of Practical Organic Chemistry*, 4th ed.; Longman: London, 1978; pp 775.
(23) (a) Evans, D. C.; George, M. H.; Barrie, J. A. *J. Polym. Sci., Polymer Chemistry Edition*, **1974**, *12*, 247. (b) Fyles, T. M.; Leznoff, C. C. *Can. J. Chem.* **1976**, *54*, 935.
(24) Elguero, J.; Claramunt, R. M.; Garceran, R.; Julia, S.; Avila, L.; del Mazo, J. M. *Magn. Reson. Chem.* **1987**, *25*, 260.
(25) (a) Regen, S. L. *J. Am. Chem. Soc.* **1974**, *96*, 5275. (b) Regen, S. L. *Macromolecules* **1975**, *8*, 689.
(26) (a) Frye, J. *Concepts Magn. Reson.* **1989**, *1*, 27. (b) Torchia, D. A. *J. Magn. Res.* **1978**, *30*, 613.
(27) Narasaka, K.; Soai, K.; Aikawa, Y.; Mukaiyama, T. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 779.
(28) Tundo, P. *Continuous Flow Methods in Organic Synthesis*; Ellis Horwood: New York, 1991.

MA9710040