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Reactivity of poly(chlorotrifluoroethylene) (PCTFE) oil and PCTFE derivatives with phenyllithium and phenyl Grignard reagents

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Summary

Poly(chlorotrifluoroethylene) (PCTFE) oil upon reaction with phenyllithium at −78°C formed functionalized products that could be isolated in three fractions by solvent extraction with pentane, ether, and tetrahydrofuran (THF). At −125°C crosslinking of polytrifluoroethylene (PF_3E), and Kel-F 800, a co-polymer of 72% chlorotrifluoroethylene and 28% vinylidene fluoride, with phenyllithium or phenylmagnesium bromide formed glassy black insoluble products. Infrared spectroscopy showed aromatic functional groups had been introduced in all the products. However, alkyl peaks were also evident in the infrared spectra of the lithiated products. Size exclusion chromatography of soluble Kel-F 800 reaction products indicated cracking to lower molecular weight material.

Introduction

Although fluorocarbon polymers are generally considered to be chemically stable, some reactions have been reported causing functionalization of polychlorotrifluoroethylene (PCTFE). A variety of alkyl, aryl or heterocyclic sulfur nucleophiles refluxed in the presence of dimethylformamide at 80°C for a week could modify PCTFE particles as the corresponding thioether (1). To increase the versatility of PCTFE particles as an HPLC column packing, Danielson and co-workers discovered that organolithium (2) and organomagnesium (3) reagents will derivatize the polymer with a variety of functional groups. The reaction of several alkyl lithium reagents such as η-butyllithium and analogous alkylmagnesium reagents with PCTFE results in loss of chlorine and the introduction of the alkyl group. Aryl lithium such as phenyllithium and arylmagnesium reagents also react in an analogous fashion with solid PCTFE particles. Dias and McCarthy (4) proposed a two-electron, elimination-addition mechanism to explain the observed reaction between methyllithium and PCTFE oil. In this mechanism (Fig. 1), a halogen-metal exchange affords the lithiated intermediate and subsequent elimination of lithium fluoride is rapid, even at low temperature (−78°C). The loss in fluorine and the gold-brown color of the reacted polymer have been attributed to the reducing capabilities of organometallics resulting in the formation of carbon-carbon double bonds (5). We have trapped the lithiated PCTFE oil intermediate formed from η-butyllithium at −125°C by quenching with dry ice to form the carboxylated η-butyl PCTFE product (6). This result also supports the mechanism in Figure 1. A similar reaction mechanism is believed to occur for organomagnesium reagents and PCTFE (6).

Although the reactions of organolithium and organomagnesium bromide have been reported in detail for solid PCTFE particles, no such reactions other than that for methyllithium at −78°C have been investigated with respect to PCTFE oil. We have found the

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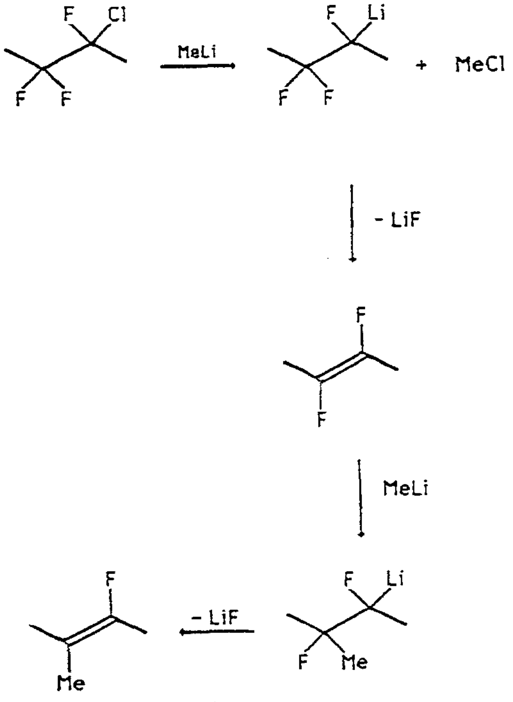
reaction of either methyllithium or butyllithium with PCTFE oil at either reflux temperatures or at −78°C in a variety of solvents generated 97-100% of only one product which was soluble in pentane (6). However, the reaction of phenyllithium or phenyl Grignard with PCTFE oil generated three products soluble in different solvents. The details of these reactions as well as the reactivity of Kel-F 800, a co-polymer of chlorotrifluoroethylene and vinylidene fluoride, and polytrifluoroethylene (PF_3E) with these aryl organometallics are reported herein. To the best of our knowledge, the potential reactivity of these latter two polymers with these reagents has not been addressed previously.

Figure 1. Two electron transfer mechanism for methylation of PCTFE oil by methyllithium (4).



Experimental

Polychlorotrifluoroethylene (PCTFE) oil-700 series was obtained from the Halocarbon Products Corp. (Hackensack, NJ). Kel-F oil #10 was obtained from Ohio Valley Specialty Chemical Co. (Marietta, OH). Kel-F 800 was obtained as a gift from the 3 M Co. (Minneapolis, MN). Based on infrared spectroscopy, elemental analysis, and size exclusion chromatography, no significant difference was found between the two types of PCTFE oil. HPLC grade inhibitor-free tetrahydrofuran (THF) as well as tetramethylethylenediamine (TMEDA) (99%), tributyltin hydride (97%), phenyllithium (in cyclohexane/diethyl ether, 70/30), and phenylmagnesium bromide (in diethyl ether) were obtained from Aldrich Chemical Co. (Milwaukee, WI). Anhydrous diethyl ether and spectral grade hexanes were obtained from Mallinckrodt Chemical Co. (St. Louis, MO). Spectral grade pentane was obtained from Fisher Scientific Co. (Springfield, NJ). Polystyrene GPC standards were obtained from Supelco (Bellefonte, PA).

Polytrifluoroethylene (PF_3F) was synthesized by reductively dechlorinating Kel-F 6061 (100% PCTFE) using tributyltin hydride (7). The soluble PF_3E was then soxhlet extracted with hexanes for one week to remove tin residues before drying to constant weight at 0.1 mm Hg.

Reactions of Kel-F Oils (Table 1)

A 2 g quantity of Kel-F in 100 mL of degassed solvent was purged using N_2 in a three-neck 500 mL round bottom flask equipped with a thermometer (or low temperature thermocouple), magnetic stirrer, condenser (where applicable), and rubber septa over a period of 30 min prior to reaction. All glassware was dried at 140°C and assembled while hot. The prepurified nitrogen purge was passed through a drying agent and molecular sieve. Positive pressure was maintained until after quenching of the reaction was complete. Reactions were equilibrated at the desired temperature prior to addition of the organometallic reagent. Organometallic reagents were added via a dropping funnel at a rate of approximately 1 mL/min. Reactions run at reflux were cooled to 0°C prior to quenching. Reactions started at less than reflux were permitted to warm to 0°C before quenching unless otherwise noted. Warming from −78°C to 0°C took approximately 2.5 hours. Dilute mineral acids were added to excess to ensure complete quenching of the reaction mixture. Quenching with methanol causes the introduction of methoxy groups into the polymer (6) and was avoided.

Following quenching, reaction mixtures were added to diethyl ether in a separatory funnel and rinsed with 4 x 100 mL of dilute mineral acid to remove salts. Acid was then rinsed free with 4 x 100 mL deionized distilled H_2O and the organic solvent removed by rotary evaporation. If the resulting polymer was found to be a solid, sufficient THF (2-3 mL) was then added to just solubilize the sample. To this solution was added excess pentane (approximately 500 mL). The solids, if present, were removed by filtration and rinsed with 100 mL of pentane. The two pentane fractions were then combined and the solvent removed by rotary evaporation to leave the polymer residue listed in Table 1 as the pentane soluble fraction. Any solids not soluble in pentane were rinsed with 500 mL of diethyl ether to remove the ether soluble fraction. Remaining solids were dissolved free from the filter paper with THF and recovered by rotary evaporation. If the polymer following rinsing and concentration was a liquid, no THF was necessary in the first step of the workup. Excess pentane was added directly and separation of the soluble fractions was carried out as outlined above.

Reactions of PF_3E and Kel-F 800 (Table 1)

Procedures were the same as those outlined above with the exception of reaction temperature, time, and the reaction mixture workup. Cooling of the reaction mixture to −125°C was accomplished using an isobutyl alcohol/liquid N_2 cooling bath. Excess liquid N_2 was added to the bath to achieve this temperature. Temperature was monitored using a low temperature type J thermocouple connected to an Omega DP900 thermocouple indicator

(Omega, Inc., Stamford, CT). Reactions were permitted to warm to 0°C before quenching. Warming from -125°C to 0°C took approximately 6 hours. Following quenching, reaction mixtures were added to diethyl ether in a 1000 mL separatory funnel and rinsed with 4 x 100 mL of dilute mineral acid and 4 x 100 mL deionized distilled H_2O. Solids were removed from the organic layer by filtration and rinsed with THF to remove soluble products. The THF rinse solution and organic layer were combined and the solvent removed by rotary evaporation. Pentane, diethyl ether and THF soluble fractions were separated as outlined previously.

Characterization of Polymers

Due possibly to competitive coupling of phenyllithium, biphenyl was a common impurity. It was removed prior to IR and NMR analyses by heating all samples to constant weight at 70°C and 0.1 mm Hg. Proton NMR spectra of soluble PCTFE derivatives were taken on a Bruker (Billerica, MA) Model WH-90 spectrometer. Infrared spectroscopy of the liquid samples was carried out on a Perkin Elmer (Norwalk, CT) Model 683 instrument. Infrared spectroscopy of the solid samples was performed on a Model MB 120-C15 Bomen (Wood Dale, IL) FT-IR instrument equipped with a microscope and diamond anvil cell.

Characterization of the polymers by size exclusion chromatography was carried out on two polydivinylbenzene columns (Jordi Associates, Bellingham, MA) connected in series. One column was 10 mm I.D. x 500 mm rated for molecules 100 - 20 x 10^6 in molecular weight (MW) and the other was 10 mm I.D. x 150 mm for molecules 10,000 - 20 x 10^6 in MW. The mobile phase propelled at 1.5 mL/min was 100% THF for all separations. The HPLC instrument was comprised of a Perkin Elmer (Norwalk, CT) Series 3 pump, a Waters (Milford, MA) U6K injector and a Waters 410 differential refractometer. All data were sent to a Waters Maxima 825 series data station. Using polymer standards ranging from 92 to 2,000,000 M.W., retention volumes were determined and a log M.W. vs. retention volume (in mL) was generated. Chromatographing samples of unknown molecular weight under the same conditions permitted calculations of number average and weight average molecular weights. Polydispersity, the ratio of weight average M.W. to number average M.W., was also calculated.

Results and Discussion

Product yields characterized with regard to solubility in pentane, diethylether, and THF generated from the reaction of PCTFE oil with phenyllithium and phenyl Grignard under a variety of conditions are shown in run #s 1-7 of Table 1. Good reproducibility of the reactions is shown by comparing runs 2 and 3. Running the reaction at reflux temperature (run #1) increased the yield of the THF soluble product. Runs 4 and 5 showed TMEDA in the reaction mixture appears to also favor the formation of the THF soluble product. Even at low temperatures, a significant amount of the THF soluble product is being formed. In addition, phenyl Grignard with Kel-F oil #700 at room temperature will cause the formation of 100% of the THF soluble product (run #6). At low temperature -125°C, the phenyl

Table I. Reactivity of Fluoropolymers with Phenyl lithium and Phenyl Grignard Reagents

				% of total recovered weight soluble in:			
Run #	X(Reagent)/ Y(Kel-F)	Solvents[a]	Temp.(°C)[b]	(Pentane	Et_2O	THF)	Insoluble Fraction[c]
1	3(PhLi)/1(Oil #10)	THF/C-hex/Et_2O	Reflux(63)	36(s)	49(s)	15(s)	0
2	3(PhLi)/1(Oil #10)	THF/C-hex/Et_2O	−78	90(s)	10(s)	0	0
3	3(PhLi)/(Oil) #10)	C-hex/Et_2 (70/30)	−78	88(s)	12(s)	0	0
4	3(PhLi)/1(Oil-700)	Trapp	−78	60(s)	26(s)	13(s)	0
5	3(PhLi)/1(Oil-700)	Trapp	−125	26(s)	49(s)	25(s)	0
6	3(PhMgBr)/ (Oil-700)	THF	d	0	0	100(s)	0
7	3(PhMgBr)/ 1(Oil-700)	Trapp	−125	78[e]	21(s)	<1(s)	0
8	3(PhLi)/ 1(Kel-F 800)	Trapp	−125	12(ℓ)	4(s)	36(s)	49(s)
9	3(PhMgBr)/ 1(Kel-F 800)	Trapp	−125	0	0	0	100(s)
10	3(PhLi)/1(PF_3E)	Trapp	−125	9(ℓ)	3(s)	11(s)	78(s)

[a] Trapp solvent consists of THF/Et_2O/Hexane (4:4:1) with TMEDA added as a complexing agent.

[b] Reactions started under less than reflux conditions were permitted to warm to 0°C (about 3 hours) before quenching unless otherwise noted. Reactions run at reflux were cooled to 0°C prior to quenching.

[c] Insoluble in pentane, Et_2O, THF, acetone, H_2O, dilute mineral acids, CH_2Cl_2, CH_3Cl, and CCl_4.

[d] (1) Cooled to 0°C before addition of Grignard reagent; (2) 12 hours at room temperature; (3) quenched with 4 N H_2SO_4 at 0°C.

[e] Extremely viscous liquid.

Grignard reagent reacts only slightly with the same Kel-F oil generating a functionalized viscous liquid and not much solid material (run #7). Although size exclusion chromatography indicated band broadening for the products (increase in polydispersity), no marked change in the MW of the products other than that due to functionalization can be concluded (Table 2). This is not surprising since the molecular weight of the Kel-F monomer unit

(116.5) and that of the monosubstituted product $-\!(FC=C-\phi)\!-$ (120) are close. The molecular weight data for the Kel-F oil based on polystyrene equivalents are considered reasonable for these types of polymers (8).

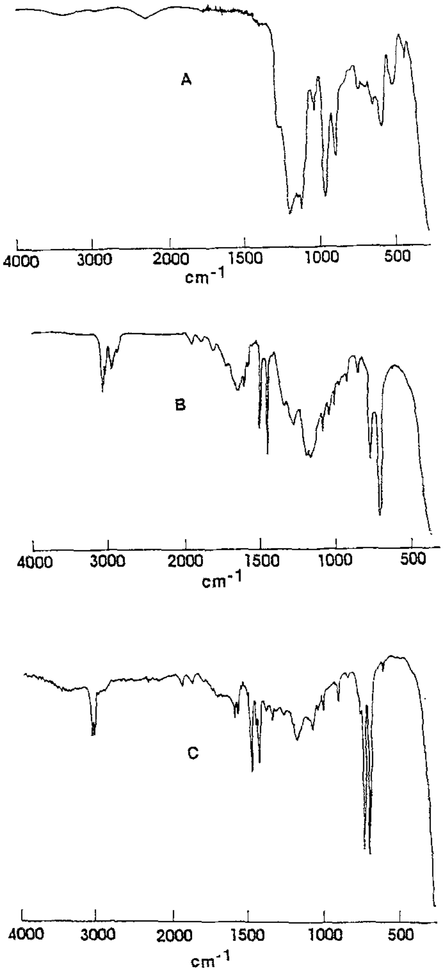
Table II. Size Exclusion Chromatography of Phenyl Derivatized Kel-F Oil and Phenyl Derivatized Kel-F 800

Reaction	Fraction	Number Ave Mol. Weight	Weight Ave Mol. Weight	Polydispersity
Kel-F Oil #10	Mean of 6 runs: (Std. dev.):	673 (5)	696 (4)	1.03
#1 (PhLi/ oil) #10	Pentane Et_2O THF	444 524 727	575 734 1106	1.29 1.40 1.52
Kel-F Oil 700		549	576	1.05
#5 (PhLi/Oil 700)	Pentane Et_2O THF	270 629 585	547 959 971	2.03 1.52 1.66
Kel-F 800	Reference 9	29,400	75,700	2.57
#8 (PhLi/Kel-F 800)	Pentane Et_2O THF	292 570 1079	398 1109 5774	1.36 1.94 5.35

The color of the pentane, ether, and THF soluble product fractions increase in darkness progressing from yellow brown to a dark brown. The dark color of all the polymer products is evidence for functionalization of the fluorocarbon polymer by the phenyl group with corresponding loss of Cl and elimination of fluorine producing the corresponding olefinic product (Fig. 1).

Infrared spectra of the polymer fractions also showed appropriate phenyl bands at 3050 cm^{-1} and a substantial loss of the C-Cl band at 950 cm^{-1} (Fig. 2B and 2C) as compared to the PCTFE starting material (Fig 2A). However, IR spectra of all the phenyllithium reacted polymer products indicated the presence of alkyl C-H peaks just below 3000 cm^{-1} as well (Fig 2B). This may be due to functionalities incorporated into the polymer as byproducts of solvent decomposition. Proton NMR was used to more accurately assess the effect of temperature on the extent of alkyl substitution in the PCTFE oils. Using integration values, run #1 (reflux) was found to contain approximately 52% aromatic hydrogens and 48% aliphatic hydrogens. Reaction 2 (−78°C) products indicated 72% aromatic hydrogens and 28% aliphatic hydrogens. This is in general agreement with the infrared spectra when one

Figure 2. Infrared spectra for A) PCTFE oil, B) phenyl PCTFE oil (pentane fraction, run #1) and C) phenyl PCTFE oil (THF fraction, run #6).



considers the varying intensities of the alkyl and aryl C-H bands. However, the IR spectrum for phenyl magnesium bromide reacted PCTFE oil (Fig 2C) showed only the aromatic C-H stretch peaks indicating solvent decomposition is not a major problem with organomagnesium reagents. Both IR spectra show almost complete loss of the C-Cl peak at 950 cm^{-1} indicating extensive functionalization. Elemental analysis for run #1 indicated only about 1.9%F compared to 17% for run #2 and 42% for the PCTFE starting material. Possibly the addition of another equivalent of organolithium reagent to the functionalized fluorolefin (F-C=C-R where R = aryl or alkyl) has occurred. This would yield, after elimination of LiF, a disubstituted olefin (R-C=C-R) exhibiting complete loss of fluorine.

The hydrogen containing Kel-F polymers (Kel-F 800 and PF_3E) showed a different reactivity with phenyl lithium and phenyl Grignard reagents. Although the same three solvent soluble fractions could be isolated for run #8 (phenyl lithium and Kel-F 800), a significant amount of completely insoluble hard, black glassy material also formed (Table 1). Reactions of phenyllithium with PF_3E causes the yield of the insoluble dark glass material to increase (run #10). The reaction at -125°C with phenyl Grignard and Kel-F 800 interestingly generates only the insoluble fraction (run #9). The same reaction occurred with PF_3E. The infrared spectra of these insoluble fractions for runs 8, 9, and 10 all indicate aryl substitution. The IR spectra of the phenyl insoluble fractions prepared from the organolithium reagent (runs 8 and 10) were virtually identical to that in Figure 2B. The IR spectrum for the product of run #9 showed less substitution and a still strong C-F band. The data in Table 2 illustrate clearly some cleavage of Kel-F 800 polymer chains is occurring as well as functionalization to generate the solvent soluble fractions. The insoluble fraction is likely due to some reaction of radical fragments to form a high molecular weight material. Free radical formation in vinylidine fluoride type polymers generating crosslinked polymers has been reported previously (10).

The significant aspect of all this work is the formation of aromatic substituted polymers which can potentially be further substituted with a variety of other functional groups (11).

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References

1. Taylor, R. T.; Pelter, M. W., (1987) J. Polym. Sci: Part C (Poly. Lett.) 25: 215.
2. Huth, J. A. and Danielson, N. D., (1982) Anal. Chem. 54: 930.
3. Danielson, N. D., Taylor, R. T., Huth, J. A., Siergiej, R. W., Galloway, J. G. and Paperman, J. B., (1983) I & EC, Product R/D, 22: 203.
4. Dias, A. J. and McCarthy, T. J., (1985) Macromolecules, 18: 1826.
5. Wu, S., (1982) "Polymer Interface and Adhesion", Marcel Dekker, NY, 280.
6. Beaver, L. G., (1987) Ph.D. Dissertation, Miami University, 1987.
7. Cais, R. E. and Kometani, J. M., (1984) Macromolecules, 17: 1932.
8. Kosmala, J., 3 M Company, Minneapolis, MN, personal communication, 1992.
9. Cady, W. E. and Caley, L. E. "Properties of Kel-F 800 Polymer", Report #UCRL-52301, Lawrence Livermore Laboratory, Livermore, CA, 1977.
10. Paciorek, K. L., Mitchell, L. C., Lenk, C. T., (1960) J. Poly. Sci. 45: 405.
11. Siergiej R. W. and Danielson, N. D., (1983) J. Chrom. Sci. 21: 362.

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