

Solvent Replacement in the Synthesis of Persubstituted Phosponitrilic Hydroquinone Prepolymer Materials

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SYNOPSIS

A desirable solvent replacement has been effected in the synthesis of persubstituted phosponitrilic hydroquinone prepolymer materials. The replacement of carbon tetrachloride with cyclohexane has no adverse effect on the composition and quality of the material prepared. The overall yield of the reaction increases from 65 to 70% and the toxicity of the reaction mixture and of the waste generated from the reaction are greatly reduced. The particularly close match of solvent properties between carbon tetrachloride and cyclohexane makes this an excellent solvent replacement. Such changes to less-expensive, less-toxic, and less-environmentally damaging solvents are on the increase. A brief list of some known replacement solvents for use in polymer and coatings applications is presented. © 1994 John Wiley & Sons, Inc.[†]

INTRODUCTION

With a growing awareness of the health and environmental hazards of many common solvents, much time and effort has been expended in the search for suitable replacements. The budgetary impact of pertinent regulatory statutes has provided some of the driving force behind such efforts. This impact is felt by both industrial and educational laboratories. Consequently, industry and academia are formulating a number of useful replacement solvents and solvent mixtures. Proposed replacements are often judged on their ability to perform the pertinent function, yet they may have very different physical and chemical properties as compared to the solvent they are meant to replace. A search of the recent literature yields a number of replacements related to polymer and coatings applications: terpenes in place of halogenated solvents in cleaning applications,¹ toluene in place of carbon tetrachloride for preparing solutions of chlorosulfonated polyethyl-

ene,² nitropropane in place of naphtha as a coating solvent,³ and *N,N'*-dimethyl-*N,N'*-propyleneurea in place of hexamethylphosphorous triamide as a co-solvent in syntheses involving highly reactive nucleophiles and bases.⁴

There are instances where a close match of physical and chemical properties is critical. The use of toluene in place of benzene is very common, starting in sophomore organic chemistry laboratories. Their solubilizing properties are similar near room temperature, yet their boiling points differ by 30°C (benzene, 80.1°C; toluene, 110.6°C), and, even more dramatically, their freezing points differ by 100°C (benzene, 5.5°C; toluene, -95°C).⁵ As a result, toluene is much more useful as a solvent for recrystallizations, both when elevated temperatures are required for sufficient solubility and when lower temperatures are required to effect crystallization.

A less well-known replacement is cyclohexane in place of carbon tetrachloride. Their freezing points differ by 30°C (carbon tetrachloride, -23°C; cyclohexane, 6.5°C), but their boiling points differ by only 4°C (carbon tetrachloride, 76.5°C; cyclohexane, 80.7°C).⁵ Because they are both nonpolar solvents, their solubilizing properties are similar for a wide range of chemical compounds. Their dielectric constants, ϵ , are very close: 2.238 for carbon tetrachlo-

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ride and 2.023 for cyclohexane at 20°C (where ϵ_{vacuum} is defined as one), with comparable temperature dependencies.⁵ Presented here is a pertinent application: the preparation of the persubstituted hydroquinone prepolymer of phosphonitrilic chloride trimer. The fundamental chemistry of phosphazenes⁶ and their utility in separations technology and membrane applications⁷⁻¹⁰ are well documented and are currently being extended in our laboratory and by others; their utility in carbon-fiber-based composite materials is also under investigation here.

The product of the reaction of hydroquinone with phosphonitrilic chloride trimer is referred to as a prepolymer rather than as a trimer because a distinct trimer molecule is not obtained. Both hydroxyl groups of the hydroquinone molecule can conceivably react with the starting phosphazene's P—Cl bonds. As a result, some hydroquinones may find themselves bridging two phosphazene rings, while others are terminally bound to only one ring. The possibility of bridging hydroquinones allows for a variety of extended structures, both cycloliner (strings of linked phosphazene rings) and cyclomatrix (networks of linked phosphazene rings) in form.⁷⁻¹⁰ Figure 1 depicts some simple bonding arrangements imaginable for this system. In contrast, the phosphonitrilic phenoxide trimer, $[\text{P}(\text{OPh})_2\text{N}]_3$,⁷ is a distinct trimer molecule because phenol does not act as a bridging group.

EXPERIMENTAL

Synthesis

The synthesis described in the patent literature makes use of carbon tetrachloride as the reaction solvent of choice in the preparation of the hydroquinone prepolymer.¹¹ We confirmed that the solubilizing properties of cyclohexane are similar to those of carbon tetrachloride for the reagents and products involved in this preparation, and that the requisite reaction times and yields are nearly identical. Further, the amount of solvent required can be half that recommended in the patent literature preparation.

In a typical synthesis, an oven-dried and argon-purged 3-L, 3-necked flask is charged with 224 g (2.03 mol) of hydroquinone (Fisher) and 80 g (0.23 mol) of the phosphonitrilic chloride trimer (Nippon Soda Co., Ltd., Tokyo) under a nitrogen atmosphere within a glove bag. With argon flowing through the apparatus, the flask is then fitted with a reflux condenser topped with a gas inlet, a 300-mL pressure-

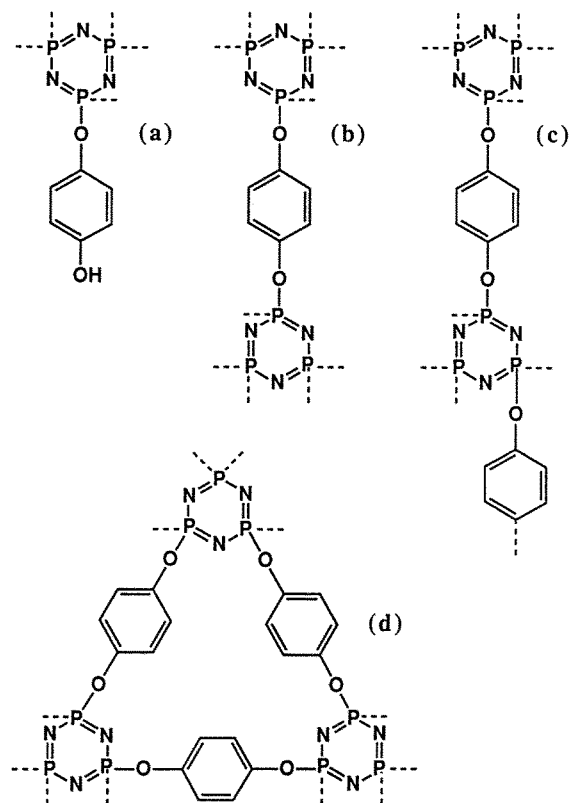


Figure 1 Possible bonding arrangements within the hydroquinone prepolymer material: (a) terminally-bound hydroquinone, (b) bridging hydroquinone, (c) cycloliner extended structure, and (d) cyclomatrix extended structure. "Cyclo-" indicates that the phosphazene ring is still intact rather than having been opened; "-linear" refers to a one-dimensional polymer; "-matrix" refers to a cross-linked polymer network.

equalizing addition funnel, and a Pyrex-clad thermocouple. First 800 mL of the anhydrous solvent (Aldrich) and then 200 mL (2.47 mol) of anhydrous pyridine (Aldrich) are transferred into the flask via cannula. A slight yellow color develops slowly upon addition of the pyridine.

Cold water is run through the reflux condenser and the gas inlet is connected to an argon bubbler to maintain atmospheric pressure within the apparatus. The reaction mixture is slowly heated to 50°C to facilitate dissolution of the reactants and thereby allow the mixture to be stirred using a large, Teflon-coated stir bar. The mixture is then heated to reflux. The mixture's yellow-to-amber color becomes stronger with time, passing briefly through a slightly yellow-green color when carbon tetrachloride is used. As the mixture nears reflux, a moderate exotherm commences and continues for a few minutes. After this exotherm subsides, it is apparent

that the reaction is nearly complete by the observable presence of a large mass of immiscible, yellow-orange syrup.

The mixture is allowed to reflux an additional 8 h to ensure complete reaction. The syrup will solidify upon cooling; this simplifies decantation of the supernatant solution. At this point the contents of the flask are not sensitive to moisture and so can be handled in air; the hydroquinone prepolymer is hydrolytically stable, as contrasted to the phosphonitrilic chloride trimer.

Isolation and purification are effected by dissolving the crude prepolymer in 500 mL of hot, 80% acetic acid (prepared from glacial acetic acid supplied by Fisher) and then precipitating the prepolymer by pouring the cooled, light amber solution into a 10- to 15-fold excess of deionized water. Digestion of the initially fine precipitate is achieved by stirring the mixture for $\frac{1}{2}$ h at room temperature. (If precipitation is attempted from a hot solution, a much finer precipitate forms that does not digest well.) The nearly white solid is collected by decantation and filtration. A second precipitation affords a white solid from a faintly amber acetic acid solution. After the second precipitation, the solid is washed until the rinsate is at a neutral pH. This washing can be performed either using a sufficiently large porous glass filter, yielding a light, white powder, or using a Soxhlet extractor, yielding an off-white, compressed mass; in the latter case potassium hydroxide is added to the water in the extraction flask to neutralize and thus trap the residual acetic acid as it is removed from the prepolymer. The solid is then dried by gentle warming; a period of 3–4 days can be necessary to drive off entrapped water unless a stream of air is passed over the solid while it is drying. No color change is observed during drying. The resultant dry mass typically weighs about 130 g, for a yield of 70% based on the limiting amount of phosphonitrilic chloride starting material when cyclohexane is used as the reaction solvent and assuming a hypothetical product of $[P(OC_6H_4OH)_2N]_3$ (see above). The yield is slightly lower (65%) when carbon tetrachloride is used.

Characterization

Elemental Analysis

Elemental analyses (C, N, and H) were performed on a Carlo Erba Instruments EA1108 CHNS-O Elemental Analyzer that was calibrated using standards with C/N/H compositions similar to that expected.

Thermogravimetric Analysis and Differential Scanning Calorimetry

Thermogravimetric analysis (TGA) was performed using a Perkin-Elmer TGS-2 Thermogravimetric Analyzer. Differential scanning calorimetry (DSC) was performed using a Perkin-Elmer DSC-2 Differential Scanning Calorimeter, temperature calibrated using ultrapure samples of indium and lead and thermally calibrated using internal circuitry.

NMR Spectroscopy

Nuclear magnetic resonance (NMR) spectra were obtained using a Bruker Instruments AC-300 300-MHz NMR Spectrometer. Spectra were obtained from dilute solutions of the prepolymer materials in acetone- d_6 (Aldrich). The internal references used were as follows: for the 1H spectra, with the spectrometer operating at 300.13 MHz, the residual proton resonance from the acetone- d_6 solvent (2.04 ppm); for the ^{13}C spectra, with the spectrometer operating at 75.47 MHz, the carbonyl carbon resonance from the same solvent (206 ppm); and for the ^{31}P spectra, with the spectrometer operating at 121.497 MHz, the single resonance from a sample of neat phosphoric acid enclosed in a capillary tube held centered within the NMR sample tube (0 ppm).

DISCUSSION

The similarity of the hydroquinone prepolymer materials obtained using the different solvents is confirmed by comparison of the results from carbon-hydrogen-nitrogen elemental analyses, TGA, and DSC, and 1H -, ^{13}C -, and ^{31}P -NMR spectroscopies.

The results from triplicate elemental analyses ($\bar{x} \pm \sigma$) are as follows: for material synthesized using carbon tetrachloride as the solvent, $50.47 \pm 0.05\%$ C, $3.51 \pm 0.03\%$ H, $6.47 \pm 0.06\%$ N; for material synthesized using cyclohexane as the solvent, $50.1 \pm 0.3\%$ C, $3.55 \pm 0.07\%$ H, $6.54 \pm 0.04\%$ N. These results are identical within experimental error and yield an empirical formula ratio of C : H : N = 27 : 23 : 3. A structural subunit composed of a trimer with three terminal and three bridging hydroquinones has a composition of 51.94% C, 3.39% H, and 6.73% N, and a ratio of C : H : N = 27 : 21 : 3. The presence of one water molecule per this structural subunit yields a composition closely in agreement with the elemental analyses: 50.48% C, 3.61% H, and 6.54% N, and a ratio of C : H : N = 27 : 23 : 3. On the basis of this hydrated structural subunit for the product, the 130 g of prepolymer obtained using

Table I NMR Spectral Data for Phosphazene Hydroquinone Prepolymer (R=OHq), Related Trimers (R=OPh and Cl), and Hydroquinone^{a,b}

	R=OHq	R=OPh ^c	R=Cl ^d	<i>p</i> -(HO) ₂ C ₆ H ₄ ^d
¹ H				
Ring Hs	6.64–6.84 (c)	6.9–7.3 (c)	—	6.66, s
Hydroxyl H	8.35 (br), s	—	—	7.65, s
¹³ C				
<u>C</u> —O—P	144, s	151, s	—	—
<u>C</u> —O—H	155, s	—	—	150, s
(— <u>C</u>) ₂ C—O—P	122, d (165)	122, d (162)	—	—
(— <u>C</u>) ₂ C—O—H	116, d (162)	—	—	116, d (157)
(— <u>C</u>) ₂ C—H	—	126, d (169)	—	—
(—C) _{2<u>C</u>—H}	—	130, d (161)	—	—
³¹ P	11.7 (c)	10.4, s	21.4, s	—

^a Data presentation: chemical shift (δ) in ppm (note on appearance of spectral line if other than sharp: br, broad; c, complex); spin multiplicity (J in Hz as necessary).

^b Spectra were obtained from dilute solutions of the materials in acetone-d₆ (Aldrich).

^c Obtained from a known sample.⁷

^d Obtained from a sample of the commercial material.

cyclohexane as the reaction solvent corresponds to a yield of 88%.

The TGA traces for these materials show four distinct regions of weight loss. The first has an onset at 60°C, amounts to less than 5% weight loss, and likely corresponds to the loss of volatile residual materials from the reaction and purification. The major weight losses, corresponding to structural degradation, are as follows: a broad loss from 300 to 400°C (10% weight loss), a sharper loss from 490 to 500°C (20% loss), and the commencement of steady weight loss above 500°C.

The DSC traces for materials prepared from either solvent show two endothermic transitions. The first is sharp, commencing at 60°C, and is due to the loss of volatile residual material from within the prepolymer sample (as indicated by TGA). The second is broader, commencing at 120°C and extending over 10–30°C, and corresponds to a melting or softening transition as indicated by both visual observation and the lack of a weight loss in this temperature region of the TGA; it should be noted that the crude prepolymer is observed to soften in hot acetic acid prior to dissolution. No other transitions are observed up to 300°C.

NMR spectral data appear in Table I; all resonances are clearly assignable. Spectral data for related materials are presented for comparison. The hydroquinone prepolymers obtained from both solvents give rise to indistinguishable resonances. The complex ³¹P resonance observed for the hydroquinone prepolymer arises because various phosphorus atoms within the phosphazene ring find themselves

in slightly different chemical environments; because both hydroxyl groups of the hydroquinone can conceivably react with P—Cl bonds, three different phosphorus environments can be envisioned, depending on the combination of terminal and bridging hydroquinones bound to the phosphorus atom (see Fig. 1). There is no evidence in the ³¹P spectra of incomplete substitution at the phosphorus atoms, that is, of any phosphorus atoms bound to either only one or no hydroquinones.

CONCLUSIONS

The replacement of carbon tetrachloride with cyclohexane as the reaction solvent is an effective means of reducing the toxicity and minimizing the amount of waste generated in the synthesis of per-substituted phosphonitrilic hydroquinone prepolymer materials. The materials obtained using cyclohexane as the solvent are indistinguishable from those obtained using carbon tetrachloride on the basis of elemental analysis, NMR spectroscopy, and TGA and DSC.

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