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13. To achieve the fundamental goal of producing a processible form of the conducting polymer polyaniline (PANI), the Phase I program concentrated on development of the synthesis of a precursor polymer via the solution co-polymerization of bis(annellated)benzoquinone with p-phenylenediamine. The resulting polymer, expected to be soluble in common organic solvents, would be converted to PANI by thermal elimination of the pendant cyclopentadiene groups following processing. Attempts to carry out the proposed polymerization reaction using conventional methods for ketone-amine condensation were not successful, and resulted in the conclusion that bis(annellated)benzoquinone is too "crowded" a ketone for the polycondensation chemistry. Simultaneously, through another line of research (motivated by the desire to produce a melt processible form of PANI which is compatible with other bulk polymers such as, e.g., polyolefins, PVC, nylon, polystyrene, etc.). UNIAX scientists discovered an alternative path to the goal of a commercially viable processible form of PANI. The basic technology, relying on "surfactant counter-ion induced processibility", is easily adapted to make processing of the conducting form of PANI possible in organic solvents. This approach was made the focus of the application for Phase II funding for the development of PANI processing technology.

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SOLUBLE PRECURSOR ROUTE
TO POLYANILINES

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Principal Investigator

Final Technical Report
January 1, 1992 to February 29, 1992

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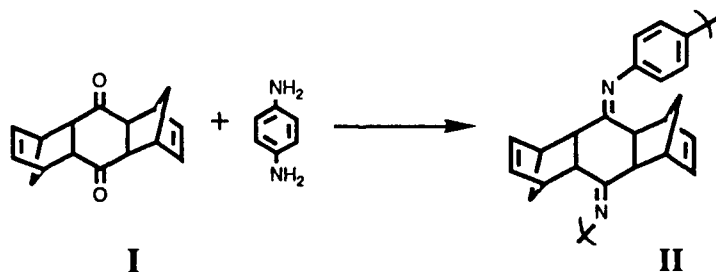
Introduction

It has been generally accepted in the field of conducting polymers that it is impossible to dope high molecular weight polyaniline (PANI) to its conducting form and thereafter dissolve the conductive form in *common non-polar or weakly polar organic solvents*. Solubility in such solvents is particularly desirable, since it would enable the creation of a variety of both conducting polyblends in which PANI is blended with bulk polymers and coatings incorporating PANI. It was for this reason that UNIAX proposed a Phase I program to circumvent the insolubility of PANI by developing a method of preparation through a precursor polymer which is soluble in the desired solvents. This strategy has required detailed study of some involved chemistry, and has not yet resulted in a synthetic route to PANI. More importantly, the initial goal for the proposed Phase I research — processibility from common organic solvents — has been achieved by an important discovery made at UNIAX in a separate project, funded by a major commodity chemicals manufacturer, initiated to develop melt processible blends of PANI with conventional thermoplastics.

Because the discovery of *surfactant counter-ion induced processibility* enables solution processing of polyaniline, in common organic solvents in its conducting emeraldine salt form, the focus of the Phase I program was immediately and appropriately shifted into this direction. The ability to process the emeraldine salt from common organic solvents opens an opportunity for the creation of a variety of industrial products (conducting coatings, paints, adhesives, epoxies, *etc.*) based on polyaniline. As a result of this important progress, UNIAX has proposed to make surfactant counter-ion induced processibility of polyaniline the basis of an extension of the original research to a Phase II effort.

Diketone - Diamine Polycondensation Towards a Soluble PANi Precursor

To achieve the fundamental goal of producing a processible form of PANI, the Phase I program concentrated on development of the synthesis of a precursor polymer *via* the solution co-polymerization of bis(annellated)benzoquinone (I) with phenylenediamine:



It was expected that the target polymer **II** would have high molecular weight and be soluble in common organic solvents. Following processing it could be converted to PANI by a retro Diehls-Alder reaction, thermally eliminating the pendant cyclopentadiene groups. Initial efforts to react **I** with *p*-phenylenediamine using conventional methods for ketone-amine condensation were not successful, but further work produced polymer under the following conditions:

Synthesis

Diketone **I** (2.40 g, 10.0 mmol) in 10 mL PhCl was added at room temp. to a stirred solution containing *p*-phenylenediamine (1.08 g, 10.0 mmol), glacial HOAc (20 mL), NaOAc (3.5 g), and PhCl (10 mL). With magnetic stirring, the solution was maintained at 50°-55°C under N₂ for 10 hours (reaction does not proceed at room temperature), after which no diketone remained as indicated by tlc (faint odor of cyclopentadiene in reaction flask). Suspension ppt.'d into 100 mL DMF, collected, dried, and pulverized in a mortar. Resulting powder washed with acetone/3% triethylamine, then water, and finally with acetone. Dried in vacuum at ambient temp. 24 hours. Yield: 1.06 g (34%). Polymer does not melt below 300°C; rather, it decomposes.

A similar yield (31%) was obtained when THF was substituted for PhCl as the co-solvent.

Characterization

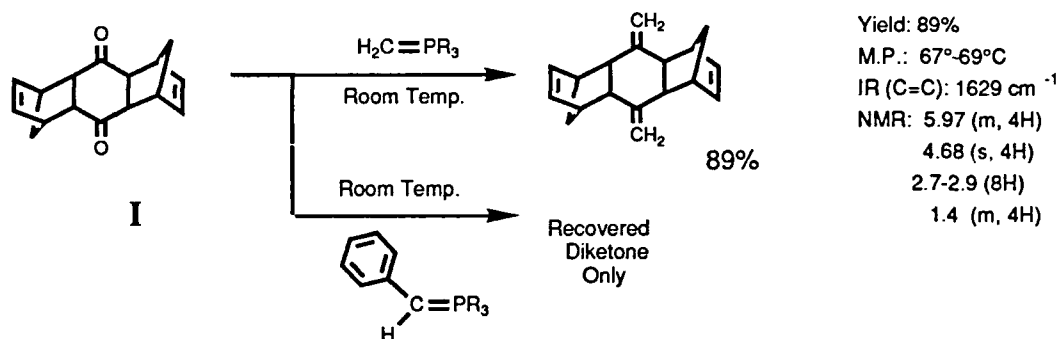
IR: Monomer I	- 1698 cm ⁻¹ (vs)	C=O
Polymer	- 1698 cm ⁻¹ (weak)	C=O
	1562 cm ⁻¹ (vs)	C=N
	1511, 1506 cm ⁻¹ (strong)	C=N
	3100-3550 cm ⁻¹ (broad)	O-H, N-H

NMR: Insufficient solubility in CDCl₃ or d₈-THF.

Elemental Analysis: Calc. for (C ₂₂ H ₂₀ N ₂) _n -	C, 84.58%; H, 6.45%; N, 8.97%
Found -	C, 73.41%; H, 5.89%; N, 7.49%
(C,H,N accounts for only 87% of powder's weight)	

The characterization results clearly indicate that the material synthesized is not the target polymer **II**. Whereas in most cases aliphatic ketones condense with aromatic amines under dehydrating conditions at room temperature, the sterically-hindered diketone **I** exhibits no such reactivity. All the above evidence implies a slow elimination of cyclopentadiene from **I**, followed by phenylenediamine condensation with the less-hindered diketone and/or cross-linking through Michael additions to the C=C (producing O-H and N-H, as seen in the IR spectra).

To test the above hypothesis, a study of the reactivity of diketone **I** was undertaken. Using very strong nucleophiles, it was found that **I** will condense with an unsubstituted methylene, but not with the more hindered phenyl-substituted methylene:



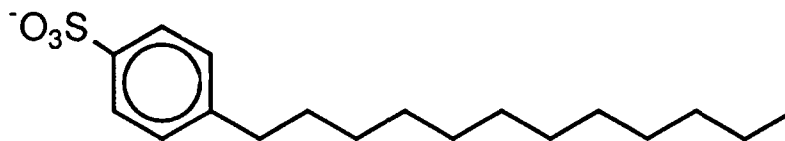
The conclusion drawn from this experiment is that diketone **I** will not undergo polycondensation with diamines. The very stark contrast in yields (89% vs. 0%) for the Wittig reactions indicates that steric considerations dominate the reactivity of diketone **I**. This inference was further supported by an unsuccessful attempt to melt polymerize monomer **I** with *p*-phenylenediamine, which resulted only in extrusion of cyclopentadiene. Attempts at "melt-polymerization" conducted in a sealed tube under vacuum produced only a black tar which, after stirring with acid, had a conductivity of $\sim 4 \times 10^{-6} \text{ S/cm}$.

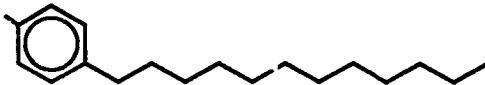
Related studies of the melt polymerization of benzoquinones with phenylenediamine were also carried out, to provide some insight into the steric and electronic factors involved in the condensation reaction. Both halogenated and unsubstituted benzoquinones underwent reaction with phenylenediamine, whereas the tetra-methyl benzoquinone ("duroquinone") formed only a reversible charge transfer complex which was broken by extraction of the phenylenediamine with acid. Finally, 1,6-hexanediamine (an aliphatic diamine) did not condense with duroquinone under melt conditions to any appreciable degree.

It appears that monomer I is too "crowded" a ketone for the polycondensation chemistry. Hence, it is clear that the goal of a commercially attractive synthetic route to a processible form of PANI is unlikely to be achieved by this strategy.

Counter-ion Induced Processibility of Polyaniline

Functionalized protonic acid solutes have recently been discovered which both dope polyaniline and, simultaneously, render the resulting PANI-complex soluble in common organic solvents. A "functionalized protonic acid" is generally denoted as $H^+(M^-R)$, where the counter-ion anionic species (M^-) is bonded to a functional group (R) chosen to be compatible with nonpolar or weakly polar organic liquids. An illustrative example is dodecyl-benzene-sulfonic acid (DBSA):



where, in this case $M^- = SO_3^-$ and $R =$ . The long alkyl chains of the dodecyl-benzene functional group lead to solubility in common solvents, such as toluene, xylenes, decalin, chloroform, *etc.*, thereby rendering PANI soluble (and, hence, processible) in its conducting emeraldine salt form.

Quite generally, counter-ion induced processibility of conducting PANI complexes can be achieved in a number of solvents through the use of an appropriate functionalizing R-group. The functional group on the counter-ion (for example the long alkyl chains of the dodecyl-benzene functional group) serves to compatibilize the PANI with solvents with similar molecular structures. In this sense, *the functionalized protonic acids act as surfactants* which enable dissolution of PANI in the solvent. Using commercially available functionalized protonic acids, UNIAX has already examined the solubility of the associated PANI complex in a variety of common organic solvents. The results of these experiments are summarized in table I at the top of the next page. This table also gives the measured conductivity of the PANI complexes (in

pressed pellets and in a few films cast from solution) obtained by doping with the functionalized counter-ion.

Table I. Solubility and conductivity of emeraldine salt protonated with various (R-SO₃H) counter-ions

R	σ (S/cm)		Xylene	CH ₃ Cl	Solubility m-cresol	formic acid	DMSO
	pellet	film **					
C ₆ H ₁₃ -	10		O	O			
C ₈ H ₁₇ -	19		O	O			
C ₈ F ₁₇ COOH	2.7		*				
C ₈ F ₁₇ -	4.8		*				
(L,D)camphor-	1.8	100-400		⊕	⊕	⊕	O
4-dodecyl-benzene-	26.4	100-250	⊕	⊕	⊕	O	
0-anisidine-5-	7.7x10 ⁻³				O	O	O
p-chlorobenzene-	7.3				O	O	O
4-nitrotoluene-2-	5.7x10 ⁻²				O	O	O
dinonylnaphthalene-	1.8x10 ⁻⁵		O	⊕	⊕		
cresol red	2.2x10 ⁻⁴ ***					O	
pyrrogallol	1.2x10 ⁻¹ ***					O	
pyrocatechol	1.9x10 ⁻¹ ***					O	

O The solubility is 0.5-2%(w/w)

⊕ The solubility is 2-15%(w/w)

* Soluble in perfluoroalkane, for example, in perfluorodecaline

** Film was cast from concentrated solution

*** pressed at 165 °C

Summary

The original strategy of this project to use polycondensation chemistry to produce a polyaniline precursor has been shown to be unsuccessful. The reason the polymerization does not proceed is likely due to steric hindrance of the monomeric diketone, as evidenced by model studies performed.

The strategy of using surfactant sulfonic or phosphonic acids as solubilizing agents for polyaniline, on the other hand, has not only been successful in every respect, but makes other attempts towards processing PANi seem awkward and obsolete. The doped PANi complexes have high conductivity and are soluble in a variety of non-polar or weakly polar solvents up to relatively high viscosities. This processing technology does not even involve synthesis (assuming

the emeraldine base is already available) but rather relies on a commercially much simpler blending technology.