

THERMOSET AND THERMOPLASTIC COMPOSITES USING POLYMER WRAPPED SWNTs AS REINFORCEMENT

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Abstract. We are developing a method for incorporating Single Walled Carbon Nanotubes (SWNT) into thermosets and thermoplastics to act as reinforcement. The helical structure of poly (m-phenylenevinylene-co-2,5-dioctoxy-p-phenylenevinylene) (PmPV) encourages this polymer to wind itself around both individual SWNTs and multiple SWNT ropes. This forms a polymer/nanotube mixture in which the polymer is mechanically anchored to the nanotube but is not chemically bound to it. Because interaction between the PmPV and SWNTs is purely mechanical, no incursion into the bond structure of the SWNTs occurs. Our current work involves the functionalization of the side chains of PmPV so that chemical binding between the PmPV and matrix can be made possible.

1. BACKGROUND

Multi walled carbon nanotubes were first discovered in 1991 as a result of research on fullerenes [1]. Several years later single walled carbon nanotubes were discovered [2]. These tubes can be described as giant molecules made from a single sheet of graphite wrapped around and joined with itself to form a cylinder whose two ends are each capped with the hemisphere of a fullerene. Multi walled carbon nanotubes are made up of several of these tubes where the smaller diameter ones are concentrically contained within the larger diameter ones. These tubes potentially have excellent fiber reinforcement properties because of their exceptionally high aspect ratios (the length of the tubes relative to their diameter) which can be as great as or greater than one million. In addition to extraordinary mechanical properties, they are predicted to have useful electronic, thermal and magnetic properties. Some of these other properties are capable of being tuned by varying the diameter and/or the chirality of the tubes [3]. All of these factors have made these

materials of great interest to a large segment of the scientific and engineering communities.

The difficulty in realizing the potential these tubes have for providing enhanced mechanical strength to polymer based composites has been their inability to homogeneously disperse, either in the polymer precursors or in the polymers themselves. A method for how to potentially change this situation occurred to us when we learned of the work by of a group in the Physics Department at Trinity College Dublin in Ireland who were able to dissolve 500 nm to 1.5 μm long multi walled carbon nanotubes in a toluene solution using the polymer PmPV [4]. They believed that they were able to get nanotubes to dissolve in organic solvents, such as toluene, because the PmPV polymer wrapped itself around the nanotube and held it in suspension in the polymer/toluene solution. They were able to get the nanotubes in solution by mixing the nanotube powder and PmPV in toluene and briefly sonicating this mixture. The structure of this polymer is a variation of the more common light emitting polymer, polyphenylenevinylene (PPV). The connecting pattern between the

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two alternating moieties making up the polymer backbone in PmPV however leads to dihedral angles in the chain causing the chain to coil, thereby forming a helical structure along the polymer's backbone. The diameter of this helix in vacuum has been calculated to be 2 nm with the pitch being 0.6 nm. The size of the helix, as pointed out by the Dublin researchers, 'fits nicely around a nanotube'.

2. OUR WORK

The objective of our work has been to develop the chemistry necessary for successfully incorporating single walled carbon nanotubes (Bucky tubes) into thermoset and thermoplastic composites in such a way that the resulting composites possess at least some of the extraordinary strength of the SWNTs. As was just explained, carbon nanotubes have been found to possess a wide variety of extraordinarily useful properties, encouraging interest, especially within the past few years, in development of the technology required to exploit these properties. Their potential for use as composite reinforcements comes from their remarkable mechanical properties. Their theoretical strength has been calculated to be more than one hundred times that of steel, and yet they are only one sixth the density of steel. They have also been found to be much stiffer than other reinforcement materials, such as carbon fibers, but are much less brittle. Their potential to produce materials with a high strength to weight ratio make them ideal reinforcement candidates for incorporation into advanced structural composites for the aerospace industry. In the long term, these materials will be used in many consumer products from automobiles to sports equipment and, because of their extraordinary mechanical properties, it is believed they will prove to be 'the ideal reinforcing fiber for composites'.

As was stated above, the primary obstacles that have been encountered with incorporating carbon nanotubes into composite materials have been the complications associated with getting them to effectively mix and uniformly disperse in the thermoset and thermoplastic composite precursors. Since single walled carbon nanotube can have aspect ratios larger than a million, they can be micrometers or even longer in length. While their extremity long length relative to their width means they should have good fiber properties, this also means they are not readily soluble in solvents. While there has been some success at dispersing shorter nanotubes in polymers, composites made with these short nanotubes having low aspect ratios have not

realized the anticipated increases in the strength of the final composite. The success of wrapping polymers around multi walled carbon nanotubes to promote the solvation of long chained nanotubes [4] suggests this technique might also be useful for effectively incorporating single walled carbon nanotubes into thermosets and thermoplastics. In solution, the polymer, poly (m-phenylenevinylene-co-2,5-dioctoxy-p-phenylenevinylene), (PmPV) spirals around the nanotubes, enveloping them. The result can be visualized as being similar to that of cryptands enveloping alkali or alkaline earth cations to make their salts more soluble. Unlike the cryptand encasement of cations however, that works through the stabilization of the positive charge on the ion, the polymer acts as a coating, providing a very different surface interface for the nanotubes to use in interacting with its environment. This new interface allows them to become solvated, or at least uniformly dispersed, in organic solvents. One of the main objectives of this work has been to find the optimum degree to which the nanotubes should be coated with these long chained polymers to make them capable of being uniformly dispersed in epoxy and nylon resins.

This work has necessarily involved the consideration of both processing and performance criteria required to make it a marketable composite. The epoxy formulations that have been investigated consist of several resins, modifiers, hardeners, and other components, all of which influence processing and performance characteristics. The result of these formulations has been important with regard to the properties achieved with the particular resins and hardeners used, and also with regard to the sequestered nanotubes solubility within the different epoxy resins. The final SWNT/PmPV composite is intended for use in high performance structural components in a host of different applications and must be versatile enough to accommodate a wide variety of manufacturing techniques. The use of the epoxy fabrication method called Resin Transfer Molding (RTM) is used for producing a wide variety of shapes, while also allowing the upscale production at competitive costs. [5] Therefore, ensuring that the composites developed here are applicable to these fabrication techniques was included in their design.

Placing various functional groups on the side chains of the PmPV polymer will make it possible to introduce covalent bonding between the PmPV and the matrix into which we are putting the PmPV/SWNT mixture. Covalent bonding will provide optimal strength in the final composites by maximizing the load transfer capabilities of the composite's

Table 1. Data from Various Epoxies Containing SWNT.

Sample #	Failure Load(lbs)	Modulus (psi)	Type Epoxy	%PmPv	%SWNT	TypeSWNT	Post Cure Temp (°C)
1	18.433	500989.92	XUMY 722	0.56	0.56	AP CAR	4h@175
2	29.456	398231.60	XUMY 722	0.56	0.56	AP CAR	4h@175
3	31.924	411551.47	XUMY 722	0.56	0.56	AP CAR	4h@175
4	27.096	445997.21	XUMY 722	0.56	0.56	AP CAR	4h@175
5	28.298	449830.10	XUMY 722	0.56	0.56	AP CAR	4h@175
6	24.276	447236.59	XUMY 722	0.56	0.56	AP CAR	4h@175
7	23.082	442819.36	XUMY 722	0.56	0.56	AP CAR	4h@175
8	21.994	430101.79	XUMY 722	0.56	0.56	AP CAR	4h@175
9	18.907	409152.00	GY6008	1.35	1.93	AP CAR	4h@175
10	13.085	354830.49	GY6008	1.35	1.93	AP CAR	4h@175
11	22.816	380019.85	GY6008	2.01	3.96	AP CAR	4h@175
12	28.094	393596.28	GY6008	2.01	3.96	AP CAR	4h@175
13	20.279	426050.82	GY6008	2.01	3.96	AP CAR	4h@175
14	22.300	290810.32	GY282	2.02	2.08	AP CAR	4h@175
15	24.308	291273.40	GY282	2.02	2.08	AP CAR	4h@175
16	37.042	394600.56	GY282	2.02	2.08	AP CAR	4h@175
17	9.462	425837.71	GY282	-	2.12	HiPco	4h@175
18	8.254	292197.44	GY282	-	2.12	HiPco	4h@175
19	11.431	421991.32	GY282	-	2.12	HiPco	4h@175

matrix to the reinforcing carbon nanotubes. This is where we are currently at with regard to this research. Following is a description of some of the mechanical properties obtained using regular, non-functionalized, PmPV with epoxies along with the latest methods developed for placing functional groups on the side chains of the PmPV.

2.1. Mechanical properties of composites

Table 1 lists the failure load (the load being applied when the composite sample fractured) and Young's Modulus (modulus of elasticity) of some of the recent experiments we have done on epoxy composites containing single walled carbon nanotubes. All of these have PmPV wrapped around the SWNT except samples 17-19. Additionally, samples 17-19 were prepared with HiPco SWNT because we wanted to know how SWNT alone would behave in our epoxy system and these were the only pure form of SWNT available to us when we did the experiment. We were unable to get the unpurified Carbolex nanotubes to disperse at this high of a loading (2.12%) without the use of PmPV. We have since acquired the ability to purify, in house, the

SWNT we get from Carbolex but, because of a problem involving air pockets becoming trapped in our epoxy systems, we don't have enough data yet with the purified Carbolex SWNT to draw conclusions. Therefore, the mechanical properties of these in house purified SWNT will not be discussed here. All of the data listed here comes from epoxy composites containing unpurified, as prepared (AP) SWNT from Carbolex, except, as has been explained, samples 17-19 which contained purified HiPco SWNT. The first cure for all of these composites was done following a two stage cure cycle of differing temperatures. The samples were first heated to 150 °C, where they remained for 2 hours, and then heated to 175 °C where they remained for 4 hours. The samples were then cooled to room temperature. No higher temperatures were used either in the first cure or the post cure because the PmPV polymer decomposes above 175 °C. All of the samples were post cured at 175 °C for 4 hours. There are three different epoxies listed in Table 1. The first is a CIBA epoxy resin called XUMY 722 (samples 1-8) that we initially chose to use for investigating our PmPV/SWNT mixture. The other two, GY6008 (samples 9-13) and GY282 (samples 14

Table 2. Data for Characterizing the Epoxy XUMY 722.

Sample #	Failure Load(lbs)	Modulus (psi)	Type Epoxy	%PmPv	%SWNT	TypeSWNT	Post Cure Temp (°C)
1	09.70	440144.00	XUMY 722	none	none	NEAT	none
2	08.77	420582.00	XUMY 722	none	none	NEAT	none
3	11.00	437349.78	XUMY 722	none	none	NEAT	none
4	09.20	286699.86	XUMY 722	none	none	NEAT	none
5	12.49	487424.00	XUMY 722	none	none	NEAT	4h@180
6	29.41	459183.16	XUMY 722	none	none	NEAT	4h@200
7	23.27	433798.88	XUMY 722	none	none	NEAT	4h@200
8	22.12	430476.25	XUMY 722	none	none	NEAT	4h@180
9	17.76	452800.97	XUMY 722	none	none	NEAT	4h@180
10	22.33	420945.63	XUMY 722	none	none	NEAT	4h@200
11	27.83	429123.57	XUMY 722	none	none	NEAT	4h@200
12	15.75	450869.99	XUMY 722	none	none	NEAT	4h@180
13	11.68	462227.14	XUMY 722	none	none	NEAT	4h@180
14	19.17	424377.24	XUMY 722	none	none	NEAT	4h@200
15	20.78	458120.57	XUMY 722	none	none	NEAT	4h@200
16	26.19	428739.42	XUMY 722	none	none	NEAT	4h@180
17	13.86	415607.86	XUMY 722	none	none	NEAT	4h@180
18	16.45	477116.71	XUMY 722	none	none	NEAT	4h@200
19	17.95	413288.55	XUMY 722	none	none	NEAT	4h@200
20	14.43	474081.79	XUMY 722	none	none	NEAT	4h@180
21	10.67	450167.59	XUMY 722	none	none	NEAT	4h@200
22	13.61	478863.82	XUMY 722	none	none	NEAT	4h@180
23	21.04	450209.74	XUMY 722	none	none	NEAT	4h@200
24	28.63	390588.77	XUMY 722	none	none	NEAT	4h@180
25	33.13	376157.71	XUMY 722	none	none	NEAT	4h@200
26	22.96	419850.40	XUMY 722	none	none	NEAT	4h@200
27	24.02	378621.00	XUMY 722	none	none	NEAT	4h@200
28	16.89	423985.00	XUMY 722	none	none	NEAT	4h@200
29	17.62	402707.49	XUMY 722	none	none	NEAT	4h@200
30	23.49	405143.55	XUMY 722	none	none	NEAT	4h@200
31	18.06	445911.00	XUMY 722	none	none	NEAT	4h@180
32	18.46	453303.04	XUMY 722	none	none	NEAT	6h@180
33	16.00	444978.32	XUMY 722	none	none	NEAT	6h@180
34	16.85	452397.42	XUMY 722	none	none	NEAT	6h@180

19), are also from CIBA and were added later after CIBA stopped manufacturing of XUMY 722. Table 2 lists data of experiments done to characterize the epoxy XUMY 722 (the first epoxy listed in Table 1) without SWNT being added. The information we determined here included finding the best cure cycle for this epoxy and how accurately we were able to calculate the Young's modulus.

A detailed discussion of our composite experiments is not given here, but from the tables it is clear that the trends indicate that PmPV/SWNT

helps the composite retain its flexural strength without decreasing the modulus, thereby increasing considerably the impact strength (the total energy capable of being absorbed before failure) of the composite relative to the epoxy alone. Also, there seems to be a definite decrease in flexural strength in composites made with HiPco but no PmPV. How the HiPco with PmPV will performed is not known at the moment because we have not yet done this experiment with high loadings of SWNTs. Notice in the later experiments in Table 1 we increased the

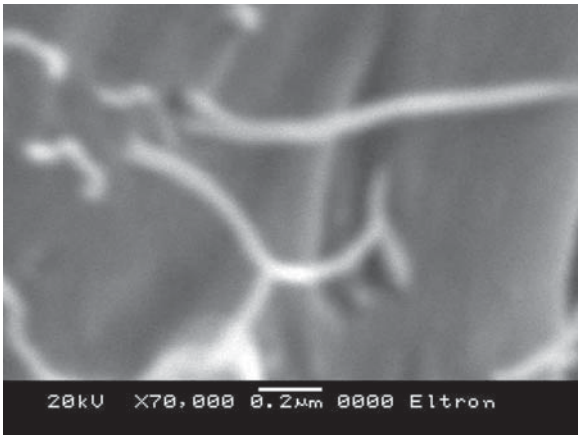


Fig. 1. This is an up close image of the epoxy that has the SWNT ropes well dispersed. The nanotubes are still present even after wiping the surface with a cotton swab soaked with ethanol. This epoxy is more conductive than the epoxy with no SWNT but not as conductive as the HiPco containing composite.

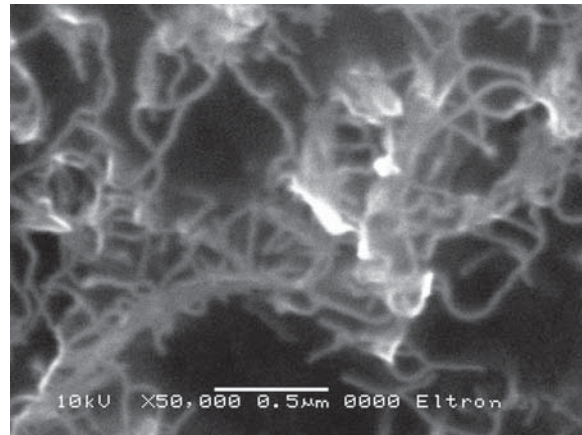


Fig. 2. The nanotubes are still in contact with one another and probably help explain the better conductivity. This also results in a very weak composite.

SWNT content. The higher percentages with the 'as prepared' Carbolex (AP CAR) nanotubes, around half of their weight is a contaminant made up of graphitic carbon with some Ni/Y catalyst so the recorded mass is of the mixture of SWNT and impurities, not the SWNT alone.

2.2. Dispersion of carbon nanotubes

Our work suggests that PmPV aids in dispersing SWNT ropes in organic liquids and epoxy precursors by separating the ropes into individual nanotubes when it wraps around them or, in some instances, by separating them into smaller ropes made up of only several nanotubes wrapped with the PmPV. This was especially evident when we used SWNT from Carbolex that had been purified in house. When these purified SWNTs were used, we were able to homogeneously disperse the nanotubes in epoxy precursors so well that in the final cured epoxy composite we were no longer able to image any SWNT ropes present on the fractured surface of the composite using SEM. With unpurified SWNT, especially when no PmPV was used, the SWNT ropes were readily seen in the SEM micrographs of the fracture surface. Fig. 1 shows the SEM micrograph of the fracture surface of a sample composite made with unpurified SWNT from Carbolex that have been wrapped with PmPV. The sample surface was washed with ethanol before imaging. It is interesting to note that this sample, with around 2% by

weight of the Carbolex SWNT (around 1% actual SWNT), did not need to be sputter coated before imaging with the SEM; even with this small amount of SWNT it was conductive on its own. Fig. 2 shows the fractured surface of the HiPco containing epoxy listed in Table 1 where no PmPV was used. This also did not need to be sputter coated, but this sample was not washed with ethanol before imaging. When this composite was washed with ethanol, all of the SWNT were removed causing the sample to require sputter coating to see the surface, otherwise the sample would charge from the electron beam probe of the SEM. The figure of this is not shown here due to space constraints, but the surface looked pock marked, as if the nanotubes had just been in contact with the surface of the epoxy but were not anchored in any way to it. This obviously is why these samples (17-19 in Table 1) fractured with such a low applied load compared to the same epoxy system with the unpurified Carbolex nanotubes and PmPV (samples 14-16 in Table 1). Fig. 3 shows the SEM micrograph of the fracture surface of an epoxy with 2% of the purified Carbolex SWNT and 2% PmPV. This composite needed to be sputter coated first before it could be imaged and yet it was one of the strongest composites tested to date. This fracture surface looks like the fracture surface of the epoxy with carbon nanotubes added. We believe the PmPV detangles the mesh-like structure of the ropes and allows them to act as individual molecules. Additionally, the PmPV supplies

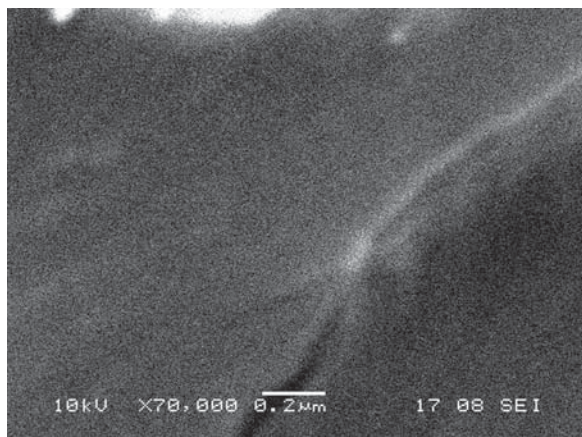


Fig. 3. There are no visible SWNT ropes in this SEM image of a fracture surface of an epoxy containing 2% by weight Purified SWNT from Carbolex mixed with the same weight of PmPV. This final composite is no longer eclectically conductive but the PmPV/SWNT mixture tested before being added to the epoxy was still very highly conductive. This may be due to the fact that only one third of the SWNT are metallic and since the ropes are now separated into individual nanotubes the percolation threshold of conductive nanotubes has not yet been reached.

a new surface to the nanotubes with which it can then interact with its environment. It is in this way that the PmPV provides a more cohesive interaction with the epoxy matrix relative to the SWNTs alone. When the PmPV is combined with the Carbolex SWNTs, (especially the purified SWNT) and to a lesser extent the HiPco SWNTs, the epoxy is less viscous and tends to flow much better relative to epoxy and nanotubes without PmPV. Also, the type of epoxy and/or hardener has an influence on how the PmPV/SWNT mixture behaves in the final composite. The little data we have on the purified Carbolex system with PmPV indicates that this source of SWNT has the most promise as far as composite strength is concerned.

2.3. Functionalization of PmPV side chains

The following is a summary of the reactions we have successfully developed to date, that are being adopted in the synthesis of the functionalized PmPV polymer. The major hurdle that needed to be overcome was finding a suitable method for protecting the double bond (the functional group we chose to

add to the side chain in this synthesis) while doing the halogen-methylation step, Step 2 of the 5 step synthesis of regular PmPV. Our strategy for doing this involved first opening the double bond by hydrohalogenation and then reclosing it using dehydrohalogenation. This all needed to be done without any reactions occurring among the other functional groups contained on our monomeric precursor and without any interference in the halogen-methylation reaction of the ring.

As is probably true in most untried syntheses, putting a functional group on the side chains of the PmPV polymer proved to be more difficult than we had first anticipated it would be. Nonetheless, we made good progress toward functionalization of the side chains of this polymer. Also, we established that a single method for the halo-methylation (Step 2 in the original PmPV synthesis) would not be possible. This was a known possible complication, so we divided this procedure into three separate procedures which we called Steps 2A, 2B, and 2C. Both Step 2A, the opening of the double bond with hydrohalogenation, and Step 2C, the reformation of the double bond through dehydrohalogenation, proved problematic. Several methods were tried [6-8] and discarded before finding a method that worked. The answer to the first problem, hydrohalogenation, was found to be hydrobromination of the double bond by bubbling HBr gas through a solution of Step 1 product dissolved in acetic acid at around 5 °C for 25 minutes. This gave a very pure product with almost a 100% yield. Chloromethylation was then performed on this new product in the same reaction used in regular PmPV synthesis. The problem that we encountered in Step 2C, the reformation of the double bond, was that the Cl on the methyl group that we added to the benzene ring tended to undergo substitution with the basic reagents used in the dehydrohalogenation. After trying many different procedures for closing the double bond [9-20], two potential pathways of solving this problem were found.

The first was to essentially do a Step 3 on the Step 2B product, thereby bypassing 2C [21]. One of the first things we determined was that we could not do Step 3 directly after 2B with triphenylphosphine, the preferred reagent, but could perform the same sort of reaction using triethylphosphite. The triethylphosphite does not form a salt with secondary halides, which is what we made in our Step 2A reaction (we get 100% Markovnikov addition of HBr to the double bond) while

the triphenylphosphine reacts with both primary and secondary halides.

The second possible reaction pathway was a de-hydrobromination using HMPA while under vacuum [18]. In our previous attempts at using HMPA, we had several things exchange with the Cl on the methyl group on the ring, one of which we were confident was the Br coming off during the reformation of the double bond. It was also determined that dimethyl amine, a byproduct formed from the HMPA during the de-hydrohalogenation, was the second thing that was exchanging with the Cl. Since HMPA boils at 230 °C, it was possible to do this reaction again, only under vacuum this time, allowing the dimethyl amine to come off (boiling point 7 °C) and preventing it from exchanging with the Cl on the ring. We have made regular PmPV with both chloromethylated monomer and bromomethylated monomer so exchange of the Cl for Br should not present a problem.

The details of how to do these reactions are given below.

1) Reaction of hydroquinone with 8-bromo-1-octene, forming Step 1 monomer precursor. 25g 8-bromo-1-octene is combined with 7g hydroquinone (approx. 0.066 mol), 8.1 g potassium hydroxide (KOH) (0.131 mol), and 250 mL N,N dimethylformamide (DMF) to form the Step 1 product of the PmPV synthesis.

8-bromo-1-octene is added to a 500 mL 3-neck round bottom flask (RBF) along with hydroquinone, both of which are rinsed with DMF (about half of the total amount). Magnetic stirring and heat are turned on. A vacuum is pulled on the reaction flask and then the flask is flushed with argon. This is repeated 3 more times. When the temperature reaches 60 °C, the KOH is added to the flask via funnel and rinsed with the remaining DMF. Reaction mixture usually turns a bright yellow after the addition of KOH. Reaction flask is evacuated nine times, and is left running, under argon, for approximately 3 hrs at 60 °C. Reaction mixture may turn a murky brown color during the course of the reaction.

To collect the Step 1 product, the DMF is decanted off the precipitate remaining in the reaction flask (mostly potassium bromide salt and a small amount of our product) and into a large sample jar with lid. De-ionized water (DI H₂O) is added to the DMF to cause the Step 1 product to precipitate out and the jar is then capped and placed in a freezer overnight. After the jar is removed from the freezer, the product is filtered using vacuum filtration, rinsing with DI H₂O, then left to dry. After product is completely dry, it is recrystallized using hexanes.

This is done by adding the product to a 500 mL heart-shaped flask with between 100-200 mL hexanes. The flask is heated with a heat gun until all the solid product melts, and then any impurities are removed from the bottom of the flask using a pipette and disposed of. The hexane mixture is left to cool, then is capped and placed in the freezer overnight. After removing from freezer the flask may be left out to evaporate the hexanes or the product can be collected using vacuum filtration.

2) Reaction forming Step 2A. Step 1 product is combined with acetic acid (usually 25 mL acid/5 g Step 1) and hydrogen bromide gas to form Step 2A product.

Step 1 is added to a 300 mL 3-neck RBF using a glass funnel through which the total amount of acetic acid is then poured in order to rinse any remaining Step 1 into the reaction flask. The Step 1 acetic acid mixture is then heated using a heat gun. After the solid is completely dissolved, the reaction flask is purged with argon for approximately 5 min, through the purge valve on the gas regulator and a gas dispersion tube that is submerged into the reaction mixture. Once the argon is turned off, hydrogen bromide gas is introduced into the reaction via the same gas dispersion tube. As the hydrogen bromide is turned on, the reaction flask is submerged in an ice bath to keep the flask cool while the hydrobromic acid reacts with the olefin. Hydrogen bromide is added continuously for approximately 20 min, then is turned off and the flask is again flushed with argon.

To recover the Step 2A product, hexanes are added to the reaction flask to dissolve most of the Step 2A product and then the contents of the flask are transferred to a separatory funnel. The funnel is shaken vigorously until all the solid product is dissolved by the hexanes and then the lower layer, containing the acetic acid, is collected into a receiving flask. The hexanes layer is washed several times with DI H₂O until its pH is neutral, then the hexanes layer is collected into a flask and the various aqueous layers are disposed of. The hexanes are then allowed to evaporate, leaving the Step 2A precipitate.

3) Reaction forming Step 2B. 2.9 g of Step 2A (6 mmol) is combined with 4.1 mL of 37% formaldehyde solution (50 mmol) in water and 2.65 mL of concentrated hydrochloric acid in 18 mL of 1,4-dioxane, with HCl gas to form Step 2B product.

Step 2A is added to a 300 mL 3-neck RBF via funnel and is rinsed with 1,4-dioxane (total amount). Magnetic stirring, heat, and water to the condenser are turned on. When 2A solid is completely dis-

solved, formaldehyde is added via funnel to the reaction flask and is rinsed with trace amounts of 1,4-dioxane. The reaction is left heating to reach 80-90 °C. When the reaction mixture has reached this temperature, hydrochloric acid is added to the reaction flask, then hydrogen chloride gas is introduced to the reaction through a gas dispersion tube. The gas is introduced to the reaction mixture continuously over approximately 18 hours.

To recover the Step 2B product, dichloromethane (CH_2Cl_2) is added to the reaction flask to dissolve the solid product, then the entire contents of the reaction flask are transferred to a separatory funnel. The CH_2Cl_2 layer containing the reaction product is extracted with DI water several times, and then collected into a beaker. The CH_2Cl_2 solvent is then removed. When the recovered solid is completely dry, it is further purified by recrystallization from petroleum ether.

4) Reaction forming Step 2C. Step 2B is combined with hexamethylphosphoramide (HMPA) to form Step 2C product.

0.5 g Step 2B is added with 10 mL HMPA to a 25-50 mL 3-neck RBF. Magnetic stirring is turned on, along with heat. Vacuum is pulled on the reaction flask, then the system is flushed with argon. This is repeated 2-3 more times. The reaction flask is heated to 75 °C and left running at 75 °C for several days while under vacuum.

To recover Step 2C, >10 mL n-hexane is added to the reaction flask, which is then shaken vigorously. The mixture is then transferred to a small separatory funnel. The hexane/HMPA mixture is extracted with DI H_2O several times, and the hexane layer is collected into a small flask where the solvent is then removed.

5) Reaction forming hydrohalogenated Step 3. Step 2B (1 mol) is combined with triethylphosphite (3 mol) to form Step 3 product.

Step 2B is added to a 50-100 mL (depending on quantity) 3-neck RBF that is equipped with a reflux condenser. The heat is first turned on, in order to melt the solid product, and the water to the condenser is also turned on. After the solid has completely melted, a vacuum is pulled several times on the system, where each time is followed by flushing with argon. Vacuum is pulled again to evacuate the reaction flask in order to add triethylphosphite via syringe. After triethylphosphite is added, the system is flushed with argon. As the system is heated to 150 °C, vacuum is pulled and the system is flushed with argon periodically. When the system reaches 150 °C, a slight vacuum is pulled on the recovery flask. The reaction runs approximately

4 hrs at 150 °C. A vacuum is pulled every 5-15 min on the recovery flask for the first hour, then every 30 min for the remainder of the reaction. After the reaction has run for 4 hrs, vacuum is opened fully to the recovery flask to remove any excess triethylphosphite.

To recover the Step 3 product, extractions with hexanes and CH_2Cl_2 with DI H_2O are used. The product seems to dissolve better in CH_2Cl_2 , although it is possible to extract with hexanes. The CH_2Cl_2 /hexane layer (depending on which solvent is used) is collected into a beaker and the solvent is left to evaporate in order to precipitate out the product.

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