

**Synthesis of a Chloroamide-Hyperbranched Polymer
Additive for Self-Decontaminating Surfaces**

**by André A. Williams, Joshua A. Orlicki, Adam M. Rawlett, and
Wendy Kosik Chaney**

ARL-TR-5990

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14. ABSTRACT The continued deployment of military assets overseas will introduce military personnel, vehicles, and other assets to microscopic pathogenic species. Bacterial infections can complicate treatment and lengthen recovery time. Development of self-decontaminating surfaces would lessen bacterial contamination by preventing bacterial growth on military vehicles and other surfaces. This project has developed spontaneously segregating multifunctional additives capable of insertion into current military coatings to reduce susceptibility to bacterial contamination of military assets.					
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1. Objective

Soldiers in Iraq and Afghanistan have suffered wounds that have become infected with various drug resistant bacteria (1, 2); and infected wounds can complicate treatment and lengthen recovery time. The goal of this project is to develop self-decontaminating surfaces that can lessen bacterial contamination by preventing organism growth on military vehicles and other surfaces that would affect Soldiers. Similar concerns exist for surfaces exposed to chemical warfare agents, which require substantial cleaning procedures to “render safe” the affected asset. To reduce logistical burdens associated with decontamination of both chemical and biological challenges, spontaneously segregating multifunctional dendritic polymer additives will be developed that are capable of insertion into current military coatings to reduce susceptibility to bacterial and chemical contamination of military assets.

2. Approach

The use of a polymer additive to modify a coating formulation is advantageous because additives can easily be integrated into existing military coating formulations without adding weight or an additional step of painting the vehicle. The additives can be designed to spontaneously segregate to the air interface as the coating cures/dries, providing a high relative concentration of the additive at the surface. Additionally, the developed additives have been developed to be fully compatible with current military formulations, and minimally impact the performance of the base coating due to their low concentration. The ideal additive must have excellent activity against a wide variety of microorganisms at low concentrations (≤ 2 weight-percent), and kill microorganisms deposited on surfaces without any action by the user (figure 1).

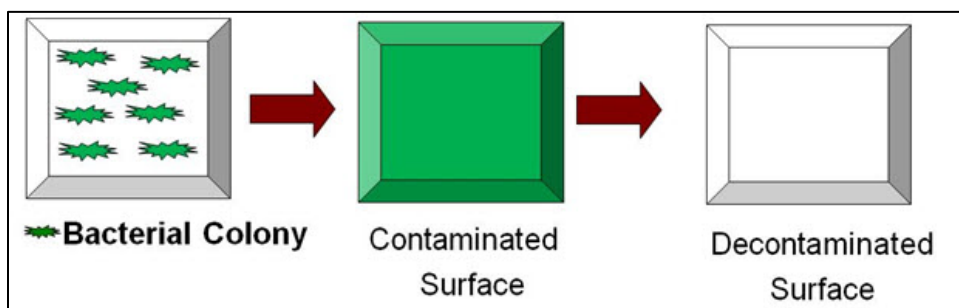


Figure 1. Self-decontaminating surface.

To achieve decontamination, the *N*-chloroamide moiety was identified as a desirable active agent. *N*-Chloroamides have been used extensively as antimicrobial and chemical

decontamination agents, and have demonstrated activity against Gram-negative and Gram-positive bacteria (2–11). The activity of *N*-chloramides is attributed to their ability to produce oxidative chlorine (Cl^+), acting as a stabilized form of bleach (10). *N*-Chloramides have been effective whether attached to polymers or integrated into textiles (8), and Worley has reported extensively on the antimicrobial properties of *N*-chloramides immobilized on fibers used as media in water filtration systems (11).

In addition to antimicrobial activity, *N*-chloroamides exhibited activity against chemical agents or stimulants of chemical agents (3–6). Salter *et al.* have reported that *N*-chloroamide modified Nomex* decomposed both 2-chloroethyl ethyl sulfide and Demeton-S, stimulants for mustard and VX[†], respectively (3). Fei and Sun reported that *N*-chloroamides oxidized the thiophosphate functional group (P=S) of various organophosphate pesticides (6). Besides the reported antimicrobial and chemical agent activity, another benefit of the hydantoin moiety is the ability to recharge the N-Cl group upon depletion by exposure to aqueous bleach (10).

Boltorn H20, a hyperbranched polymer (HBP), served as the core polymer in this study. HBPs were chosen because of their highly branched structure and a large number of reactive end groups at the periphery of the molecule. Due to this structure, HBPs provided a flexible platform for the preparation of multi-functionalized materials and provided a high local concentration of desired groups to the surface.

Boltorn H20 polymer was insoluble in most organic solvents but soluble in high boiling solvents such as dimethylsulfoxide (DMSO), pyridine, *N,N*-dimethylformamide (DMF), and 1-methyl-2-pyrrolidinone (NMP). These solvents can be difficult to remove upon the completion of reactions; therefore, melt condensation was the preferred method of modification for the base Boltorn H20 polymer. Three groups were attached to the Boltorn H20 core. These groups included lauric acid, which provides aliphatic chains to increase the solubility of the core polymer; perfluorinated octanoic acid (PFOA) was attached to provide a thermodynamic driving force to transport the polymer to the surface of the substrate and then 5,5-dimethylhydantoin was attached to provide antimicrobial and chemicidal activity.

Following synthesis and the characterization of products with proton NMR (¹H NMR), carbon 13 NMR (¹³C NMR), and infrared (IR) spectroscopy, x-ray photoelectron spectroscopy (XPS) analysis was used to determine the near-surface elemental composition, which allowed an assessment of both HBP concentration and surface segregation. HBPs were integrated into Estane 58237 films, and XPS was used to analyze carbon, nitrogen, oxygen, fluorine, and chlorine content at the film surface. High fluorine content translated into high polymer content at the film surface. Chlorine detection indicated the presence of the chloroamide group, and evaluated any in situ chlorination reaction or *N*-chloroamide regeneration.

*Nomex is a registered trademark of DuPont.

† O-ethyl S-[2-(diisopropylamino)ethyl] methylphosphonothioate.

3. Results and Discussion

3.1 Synthesis of Chloroamide-Boltorn Polymer

Synthesis of the chloroamide-Boltorn H20 polymer was accomplished in four steps (figure 2); although, a three step synthesis could be viable if the hydantoin moiety was chlorinated after incorporation into films. The first step attached the lauryl and perfluorinated groups via a melt condensation. Following this reaction, 40% of the peripheral alcohol group of the HBP should have been converted into ester groups, which left the remaining 60% of the alcohol groups available for the subsequent reaction. The second step attached the chloromethylene unit via acid halide chemistry. The third step attached the 5,5-dimethylhydantoin group via bimolecular nucleophilic substitution (S_N2) chemistry. The final chlorination step used bleach or trichloroisocyanuric acid (TCCA).

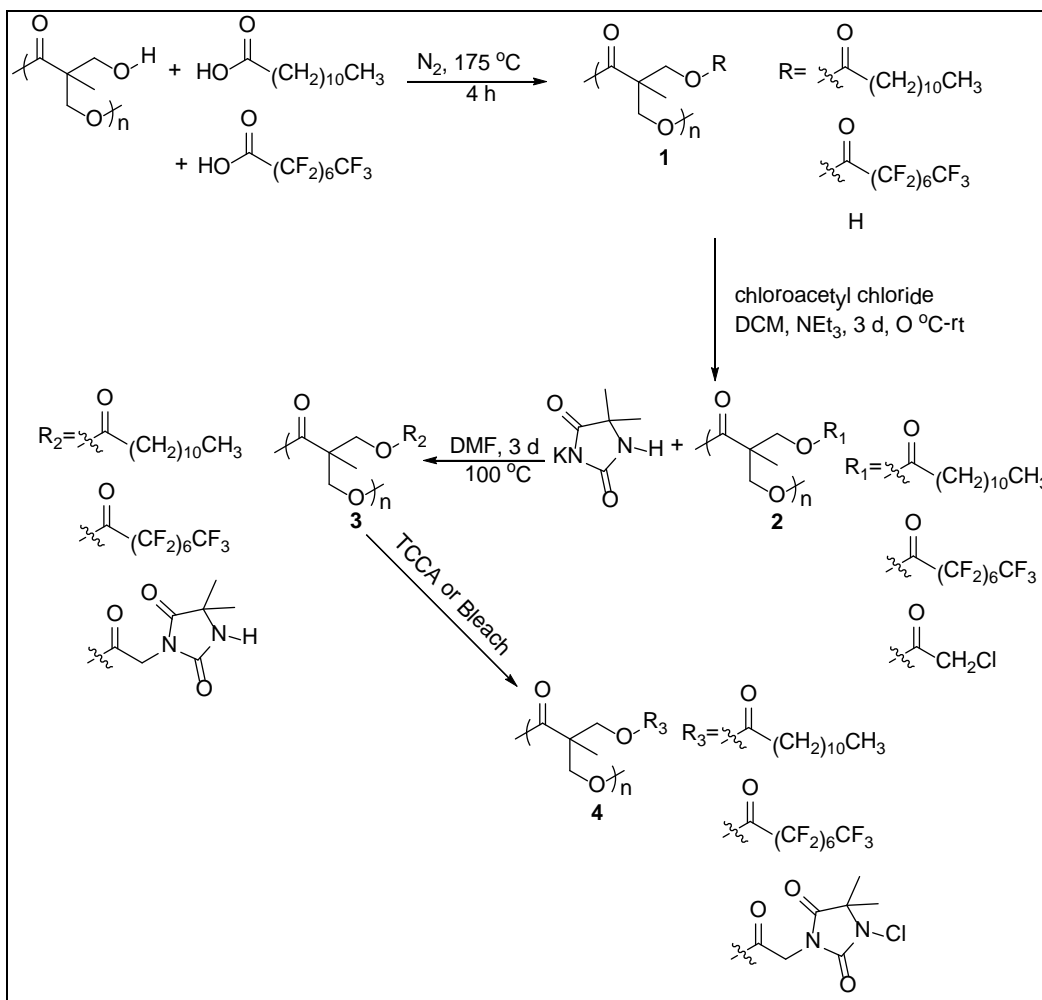


Figure 2. Synthesis of chloroamide-Boltorn H20 polymer.

3.1.1 Synthesis of Polymer 1

The lauryl and perfluorinated groups were attached to the Boltorn H20 polymer via melt condensation (figure 3). Boltorn H20 (6.00 g, 51.7 mmol) and lauric acid (2.07 g, 10.3 mmol) were melted, and then stirred under N₂ for 15 min at 175 °C. After 15 min, PFOA (4.28 g, 10.3 mmol) was added and reaction was allowed to proceed for 4 h. The reaction produced an orange viscous oil in 85% yield. The reaction product was dissolved in dichloromethane (DCM) (30 mL) and the solution was dried with anhydrous sodium sulfate (Na₂SO₄) before being used in the next step without further purification (figure 4). ¹H NMR (CDCl₃)[‡], δ ppm: 0.89 (t, 3H), 1.08–1.45 (m, 27H), 1.60 (s, 2H), 2.32 (s, 2H), 3.36–3.98 (m, 15H), 3.98–3.48 (m, 11H).

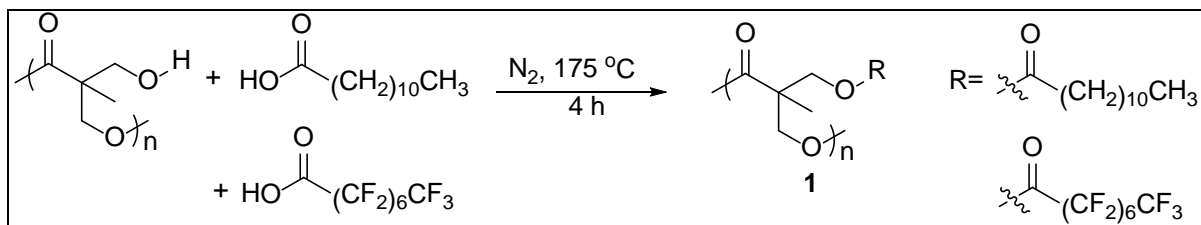


Figure 3. Melt condensation of Boltorn H20, PFOA, and lauric acid.

[‡] Deuteriochloroform.

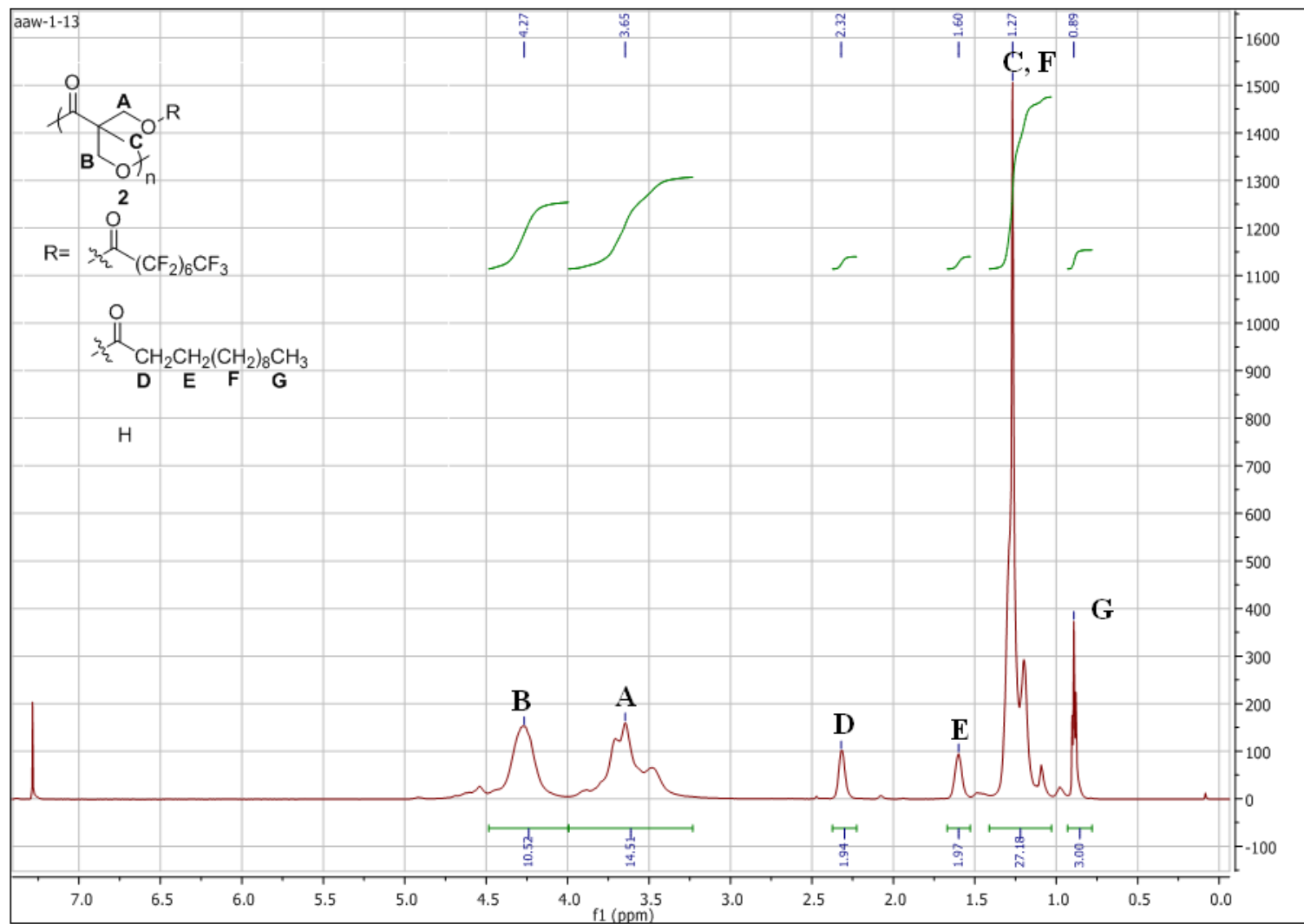


Figure 4. ^1H NMR spectrum of polymer 1. For NMR purposes, because of the dendritic structure and the way the molecules were functionalized, the main chain and end group protons cannot be distinguished.

3.1.2 Synthesis of Polymer 2

In the next step, the chloromethylene group was attached to polymer **1** via acid halide chemistry (figure 5). The dried DCM solution from the previous step was filtered into a 3-neck round-bottom flask and stirred in an ice bath under nitrogen (N_2). Triethylamine (3.66 g, 36.2 mmol) was added to the round-bottom flask, followed by the slow addition of chloroacetyl chloride (4.09 g, 36.2 mmol) via syringe. The reaction mixture was allowed to warm to room temperature (rt) and stirred for 3 days (d). The reaction mixture was then filtered into a separatory funnel. The organic solution was washed with water, 2% aq HCl, and brine. The organic phase was dried with Na_2SO_4 , filtered, and then concentrated using a rotary evaporator. The resulting viscous orange liquid was dried under vacuum at $60\text{ }^\circ\text{C}$, and resulted in 83% yield. ^1H NMR ($CDCl_3$), δ ppm: 0.86 (t, 3H), 1.08–1.45 (m, 33H), 1.57 (s, 2H), 2.28 (s, 2H), 3.35–3.86 (m, 12H), 4.09 (s, 7H), 4.14–4.45 (m, 19H). ^{13}C NMR ($CDCl_3$), δ ppm: 8.44, 14.05, 17.24, 17.64, 18.10, 19.02, 20.63, 22.61, 24.79, 29.07, 29.20, 29.26, 29.40, 29.53, 31.84, 33.96, 34.12, 40.62, 45.78, 46.50, 48.56, 52.95, 53.47, 54.67, 61.62, 63.30, 64.38, 64.78, 65.09, 65.75, 66.30, 66.47, 66.66, 67.15, 68.74, 69.12, 69.65, 70.25, 70.56, 71.01, 71.63, 72.70, 93.79, 160.30, 162.1, 162.3, 162.5, 166.9, 167.3, 167.7, 171.5, 171.8, 173.1, 173.8.

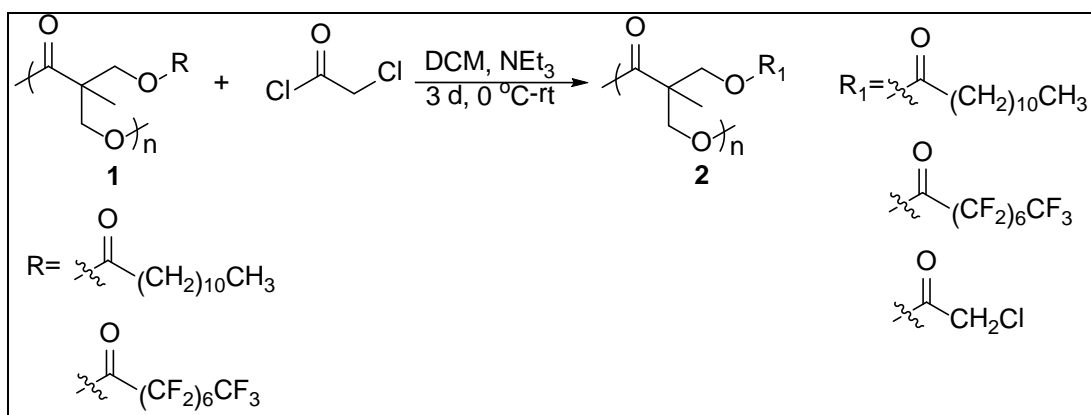


Figure 5. Attachment of chloromethylene group to modified HPB.

^1H NMR (figure 6) and ^{13}C NMR (figure 7) supported the formation of the desired product. The ^1H NMR showed the presence of the chloromethylene peak (figure 4, Peak B). Prior to this reaction, 60% of the alcohol groups should be available for further modification. However, even when a large excess of the acid halide was used, a significant amount of unreacted alcohol groups (figure 4, Peak A) remained in the reaction product. This signified that the previous melt condensation reaction did not attach the desired quantity of lauryl and perfluorinated ester groups. Nonetheless, the reaction product was used in the subsequent reaction.

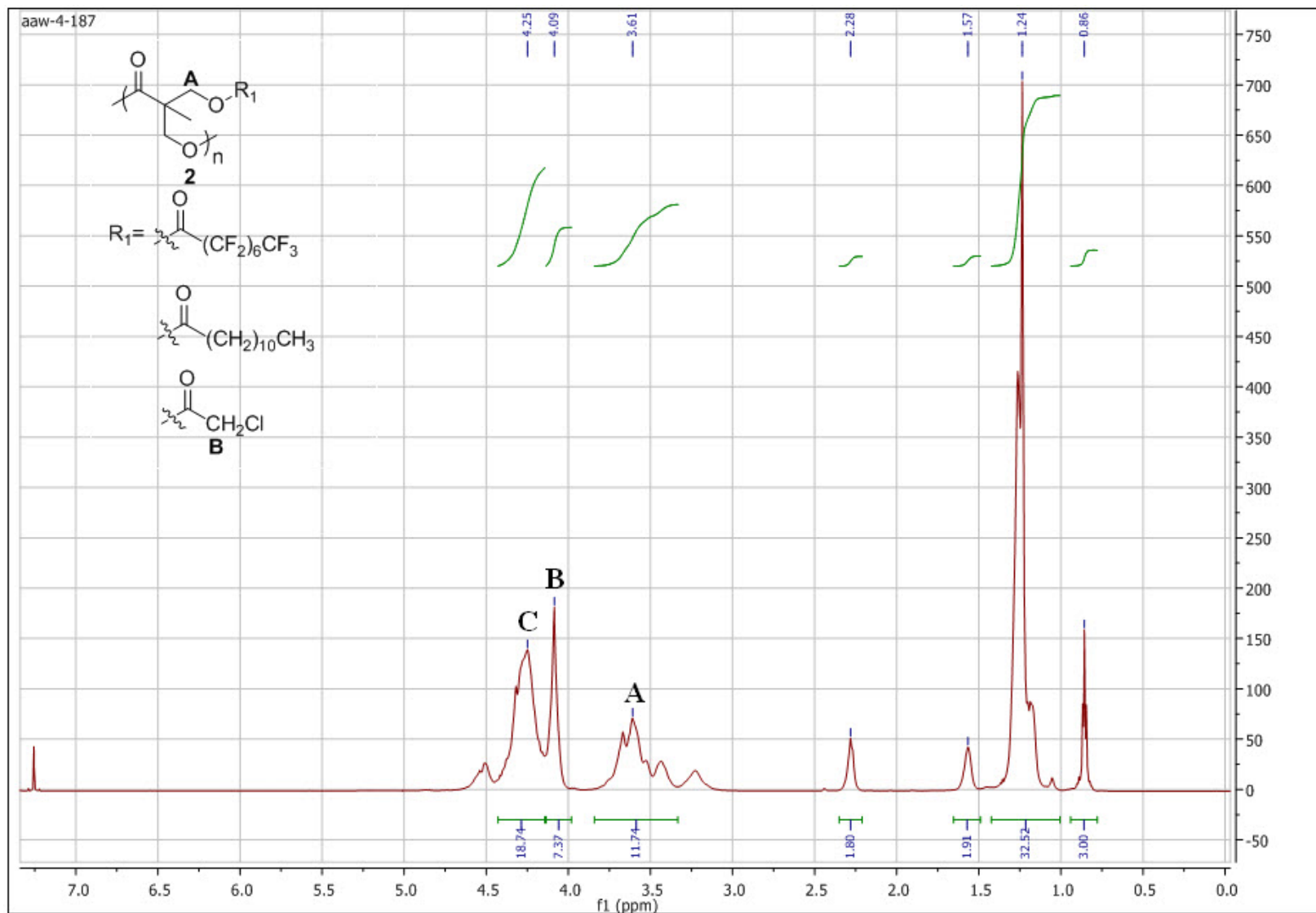


Figure 6. ^1H NMR spectrum of polymer 2.

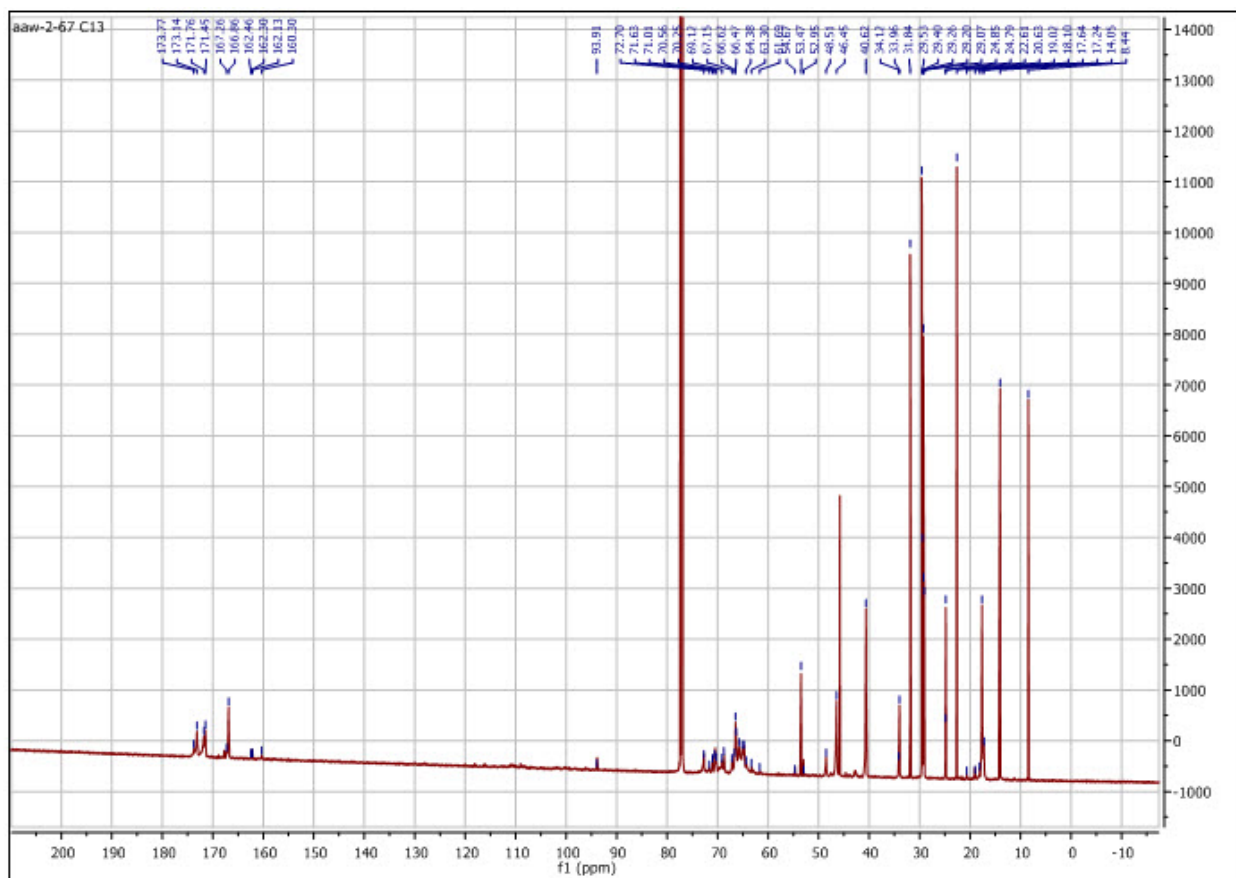


Figure 7. ^{13}C NMR spectrum of polymer **2**.

3.1.3 Synthesis of Polymer 3

The hydantoin group was attached to polymer **2** via $\text{S}_{\text{N}}2$ chemistry in the third step. 5,5-Dimethylhydantoin potassium salt (1.79 g, 10.8 mmol) was dissolved in DMF (20 mL) at 60 °C. Polymer **2** (3.19 g, 16.6 mmol) was dissolved in DMF (10 mL) and added to the round-bottom flask. The reaction mixture was then stirred for 3 d at 100 °C. Following completion, the solvent was purged with N_2 . The polymer was redissolved in DCM, and then washed with water. The organic layer was dried with anhydrous Na_2SO_4 , filtered, and then concentrated with a rotary evaporator. The polymer was dried under vacuum at 100 °C, and resulted in 71% yield. ^1H NMR (CDCl_3), δ ppm: 0.89 (t, 3H), 1.01–1.36 (m, 26H), 1.46 (s, 20H), 1.59 (s, 2H), 2.31 (s, 2H), 3.36–3.80 (m, 6H), 3.98–4.55 (m, 20H). ^{13}C NMR (CDCl_3), δ ppm: 14.05, 17.56, 22.60, 24.72, 29.06, 29.20, 29.25, 29.39, 29.52, 29.88, 30.40, 31.82, 33.94, 34.13, 39.15, 46.37, 48.46, 53.47, 59.18, 64.77, 66.24, 68.63, 69.12, 70.47, 71.01, 72.75, 93.82, 155.34, 166.8, 167.1, 167.7, 171.5, 171.8, 172.0, 173.1, 173.8, 177.0.

The reaction was successful and led to the complete consumption of the chloromethylene group. Relative to the ^1H NMR (figure 6) and ^{13}C NMR (figure 7) of polymer **2**, both ^1H and ^{13}C NMR (figures 8 and 9 respectively) support the formation of polymer **3**. The ^1H NMR spectrum revealed the disappearance of the chloromethylene group in the starting material (figure 6, Peak B) and the emergence of the methyl group (figure 8, Peak B) of the hydantoin moiety. Additionally, the integral ratio between peaks A and B (figure 8) relative to the integral ratio of starting material (figure 6, Peaks A and C) increased, which indicated the methylene group next to the hydantoin moiety was located under Peak C. ^{13}C NMR also supported product formation as the hydantoin carbonyl groups emerged in the spectrum of the product that was not present in the starting material (figure 9, Peaks A and B).

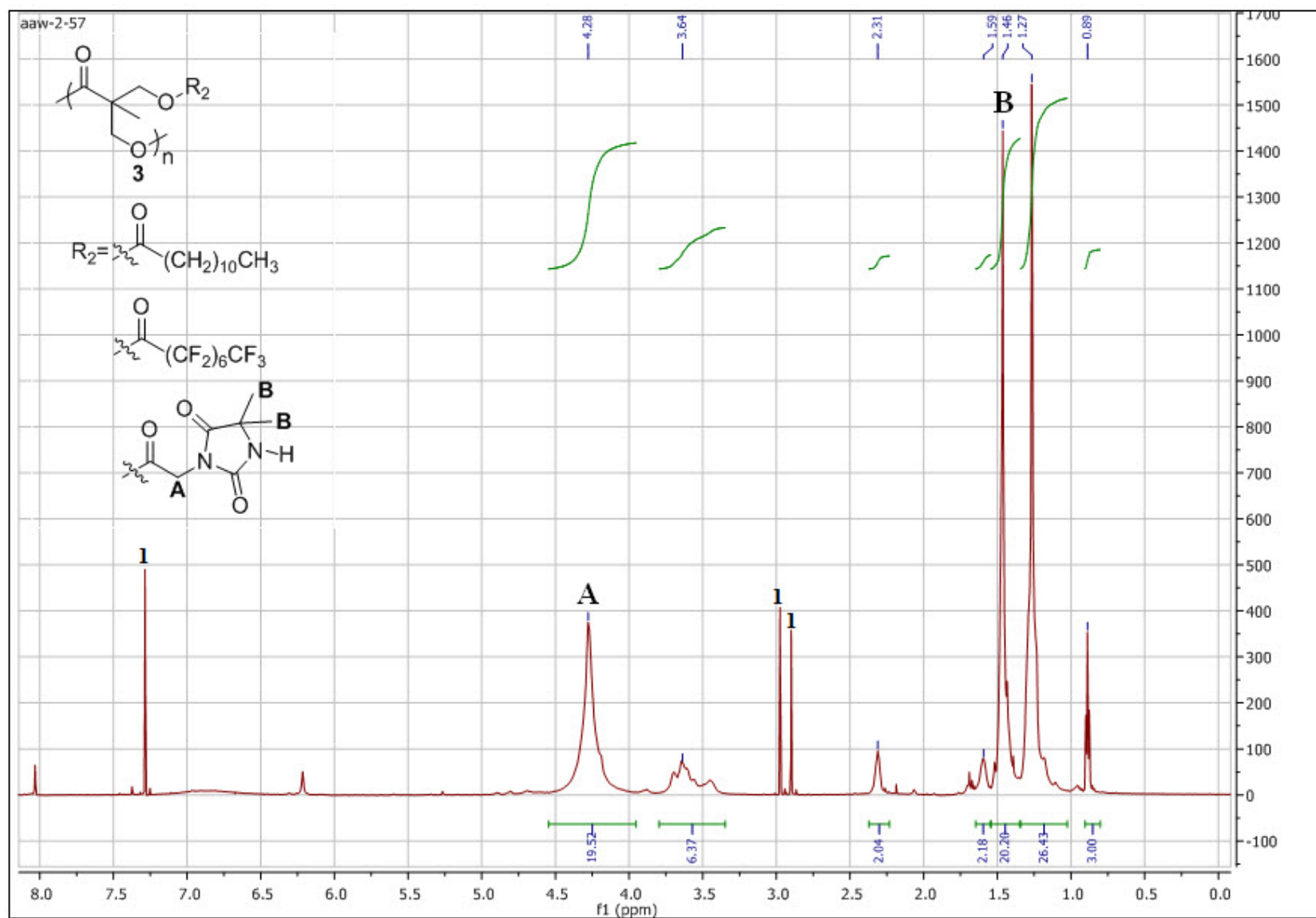


Figure 8. ^1H NMR spectrum of polymer 3. Peaks 1 correspond to DMF.

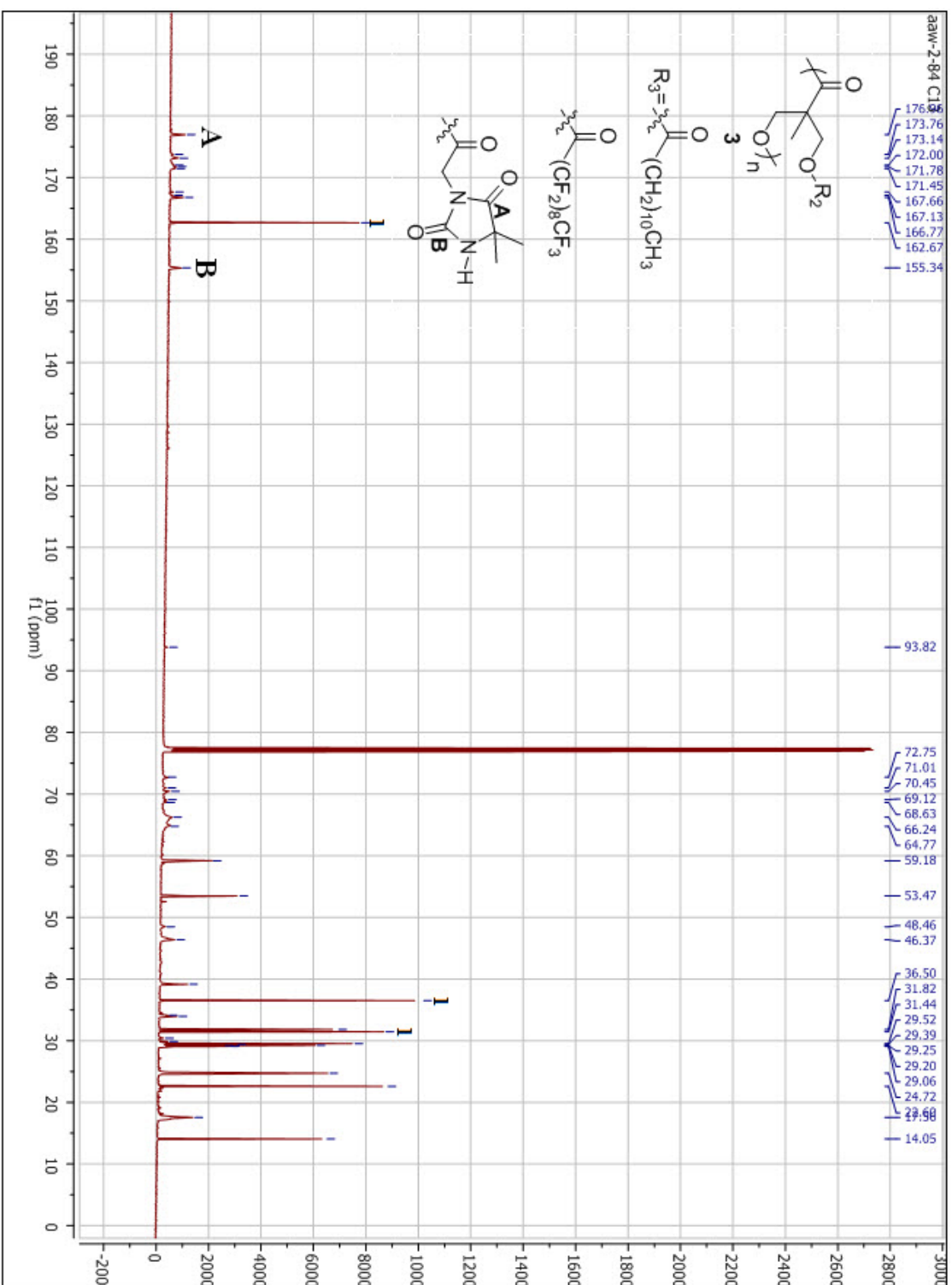


Figure 9. ^{13}C NMR spectrum of polymer **3**. Peaks **I** correspond to DMF.

3.2 Preparation and Chlorination of Hydantoin-Boltorn Films

The nonchlorinated hydantoin-Boltorn H2O polymer **3** was incorporated into Estane and poly(methyl methacrylate (PMMA) films and chlorinated with 13% aqueous bleach. Bleach treatment was reported as a viable means to chlorinate the hydantoin groups (10); however, these attempts mainly centered on the chlorination of fibers. Bleach converted the N-H bond of the hydantoin group into an antimicrobial N-Cl group. The following experiments were designed to evaluate the viability of recharging surfaces with aqueous bleach.

Polymer **3** was incorporated into both Estane 58237 and PMMA films. Polymer **3** was dissolved in tetrahydrofuran (THF) to afford 2% solutions. The solutions were cast on glass cover slips and allowed to dry in a desiccator overnight at ambient temperature, and then dried overnight at 50 °C. Following the preparation of the films, two chlorination methods were employed. For the first “soaking” method, films were soaked in bleach for 3–60 min. Estane films could only be soaked for 30 min due to film detachment for longer soaking times, and became wrinkled and did not retain the initial flat appearance. However, PMMA films were soaked for 1 h without any notable distortion. A second “standing” method was used in which bleach was deposited on the film surface and allowed to stand for 30 min (Estane films) or 1 h (PMMA films). Following bleach treatment, films were immediately soaked twice in water for 2 min. Attempts to soak the films in water for a third time often led to film delamination in Estane films. The films were then dried overnight in a 50 °C oven.

3.2.1 XPS Analysis of Hydantoin-Boltorn Estane Films

XPS (table 1) was used to analyze Estane films infused with polymer **3** (AAW samples). Films were soaked in a 13% bleach solution for 3 or 20 min to determine the minimum length of time needed for chlorination. The time allotted for bleach treatment did not affect Cl uptake. Samples (AAW-2-102.3 and AAW-2-102.20) soaked for 3 and 20 min respectively, did not display any substantial difference in Cl at the surface of the film. Additionally, these samples had similar Cl levels as the control Estane films (Estane 2 and Estane 3). Therefore, Estane, not the hydantoin moiety, was likely responsible for Cl uptake. Since the bleach treated films did not display markedly increased chlorine content relative to the control samples, the chlorine content cannot be attributed to the chlorination of the hydantoin moiety.

Table 1. XPS analysis of the chlorination of hydantoin-Boltorn H2O Estane films.

Films	Soaking Method (Minutes)	% of Elements				
		C	F	O	N	Cl
Estane 1	0	82.6	0.27	14.77	2.36	0.00
Estane 2	3	82.77	0.00	15.1	1.80	0.33
Estane 3	20	84.45	0.00	13.26	1.85	0.44
AAW-2-102	0	76.44	0.91	20.97	1.66	0.02
AAW-2-102.3	3	74.11	0.97	22.56	2.10	0.26
AAW-2-102.20	20	74.17	0.51	23.65	1.29	0.38

3.2.2 XPS Analysis of Hydantoin-Boltorn PMMA Films

Following the discovery that Estane films retained chlorine, polymer **3** was integrated into PMMA films and bleach was deposited on the film surface and allowed to stand 1 h. XPS (table 2) analyzed the success of bleach treatment of hydantoin-Boltorn films. Both soaking and surface methods were used in chlorination experiments.

Unlike Estane, PMMA control films did not retain chlorine nor became wrinkled following bleach treatment. Unfortunately, following bleach treatment, the surfaces were not chlorinated. Additionally, the surfaces lost fluorine content. Neither soak nor standing methods yielded chlorinated surfaces and both methods resulted in the loss of fluorine content. These results indicated that bleach treatment was not a viable option for PMMA and Estane surfaces. The failures encountered while attempting to chlorinate both Estane and PMMA surfaces question the viability of bleach rechargability of non-fiber surfaces.

Table 2. XPS analysis of the chlorination of hydantoin-Boltorn H2O PMMA films.

Films	Bleach Treatment (minutes)	Atomic Concentration					
		Si	C	N	O	F	Cl
PMMA	0	0.31	74.4	0.00	25.3	0.00	0.00
AAW-2-102	0	0.16	72.6	1.82	24.9	0.56	0.00
AAW-2-153	0	0.00	70.9	1.38	26.2	1.22	0.28
Soaking Method							
PMMA	60	5.33	70.3	0.00	24.4	0.00	0.00
AAW-2-102	60	0.51	73.7	0.74	25.0	0.00	0.03
AAW-2-153	60	0.88	73.9	0.65	24.5	0.00	0.01
Standing Method							
PMMA	60	1.43	74.2	0.00	24.4	0.00	0.00
AAW-2-102	60	2.18	72.8	0.58	24.4	0.00	0.09
AAW-2-153	60	0.25	72.5	0.39	26.9	0.00	0.00

3.3 Chlorination of Hydantoin Group with TCCA

Following the difficulties of surface chlorination with bleach, TCCA was used to chlorinate the hydantoin group. Researchers routinely used TCCA to chlorinate various amines (12), as well as the hydantoin moiety (13, 14). This approach was desirable because it would eliminate the need

to treat surfaces with bleach, which resulted in surface degradation. Additionally, the use of TCCA, unlike bleach, enabled reactions in organic solvents. Two separate TCCA chlorination reaction conditions were used in DCM (13) and acetonitrile (14) (figure 10).

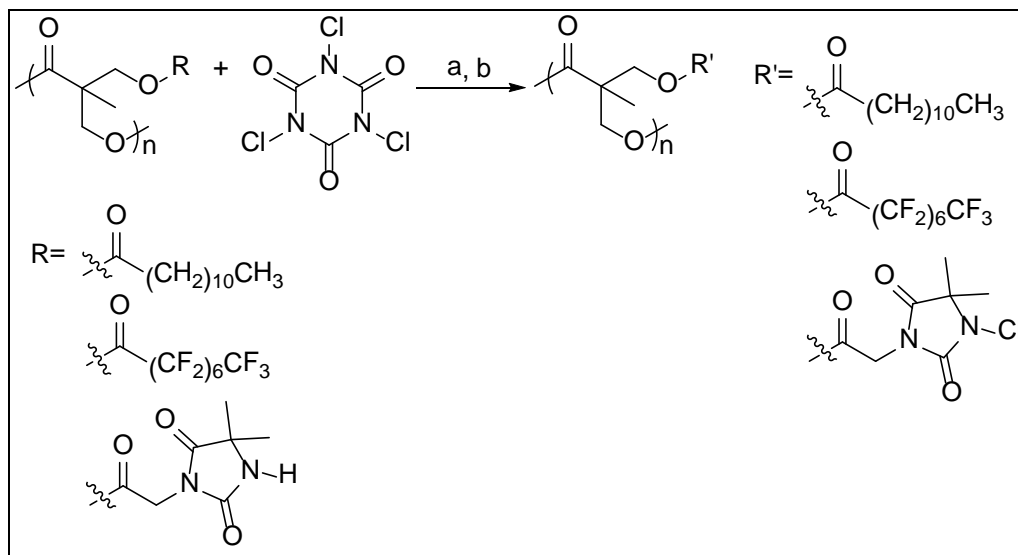


Figure 10. TCCA chlorination of hydantoin-Boltorn H20 polymer. Reaction condition a = DCM, 0 °C–rt, 24 h; b = acetonitrile, rt, 24 h.

3.3.1 TCCA Chlorination in DCM

Polymer **3** (1.00 g, 3.52 mmol) was dissolved in DCM (10 mL) and the solution was stirred in an ice bath. TCCA (0.57 g, 2.46 mmol) was added slowly and the reaction mixture was allowed to warm to rt and stirred for 24 h. After 24 h, the reaction mixture was placed in an ice bath and stirred for 15 min. The reaction mixture was filtered, and then the filtrate was concentrated using a rotary evaporator. The product was stirred overnight in isopropyl alcohol (IPA). The resulting mixture was filtered, and the filtrate was then concentrated using a rotary evaporator. The product was dried under vacuum overnight at 100 °C.

3.3.2 TCCA Chlorination in Acetonitrile

Polymer **3** (0.998 g, 3.51 mmol) was dissolved in acetonitrile at rt. TCCA (1.06 g, 4.57 mmol) was dissolved and resulting solution was stirred overnight. After 24 h, the reaction solution was concentrated using a rotary evaporator. The resulting yellow solid was redissolved in IPA and the insoluble white paste was removed via filtration. The IPA-filtration step was repeated until no precipitation occurred.

3.4 Results of TCCA Chlorination

The acetonitrile reaction yielded a reaction product that was mostly clean with some impurities in 2.8–3.2 ppm (figure 11). The DCM reaction yielded a reaction product that had DCM and DMF (from the starting material) impurities (figure 12). Unfortunately, product characterization

for both reaction products was difficult using the ^1H NMR because the N–H peak in the starting material was not visible. Therefore, ^1H NMR could not be used to determine if the conversion of N–H into N–Cl was successful.

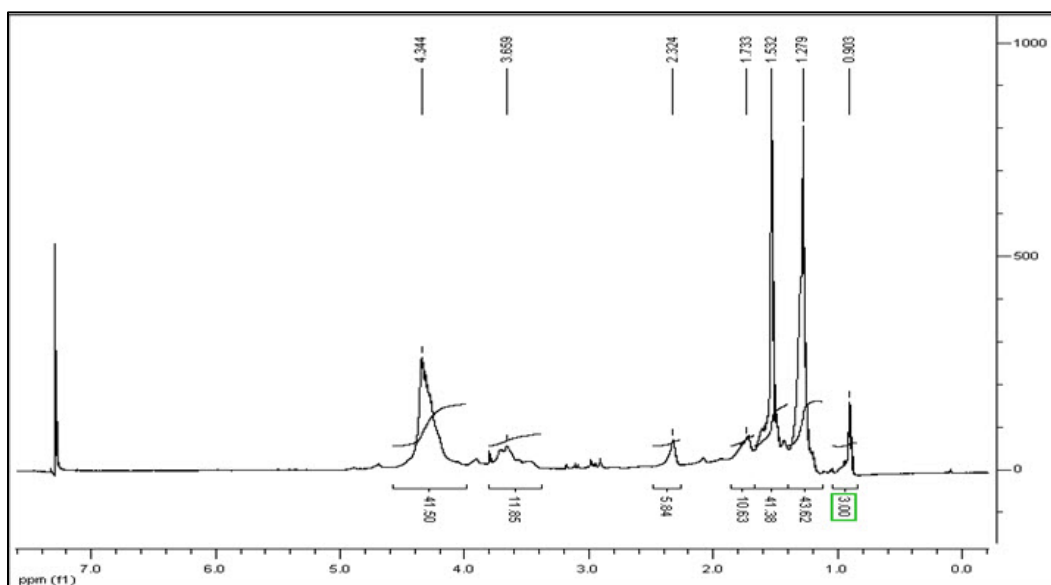


Figure 11. Chlorination of polymer **3** in acetonitrile.

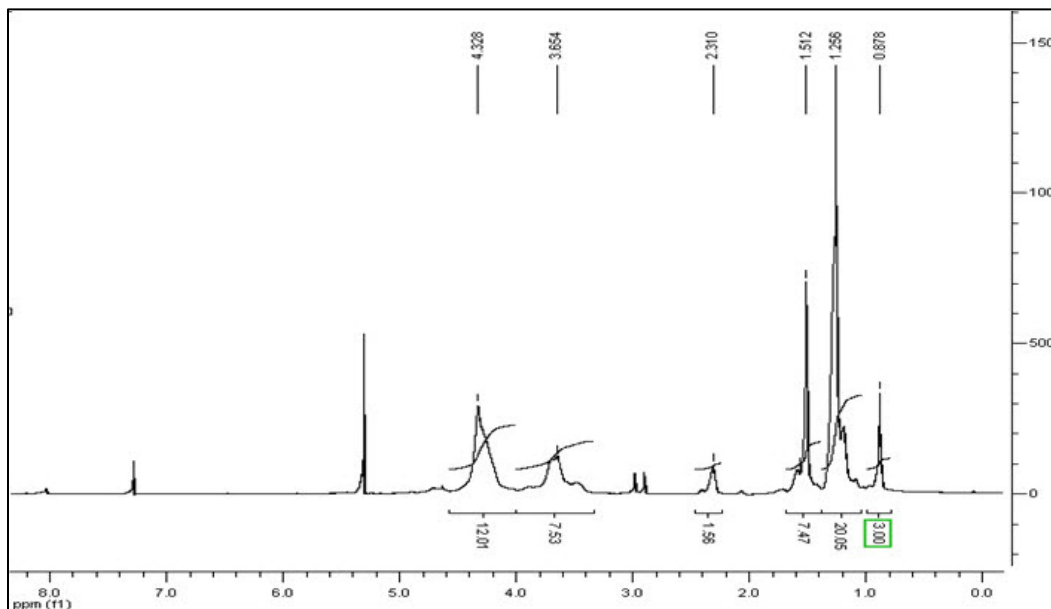


Figure 12. Chlorination of polymer **3** in DCM.

IR was used to evaluate whether the TCCA chlorination reactions were successful. To help in this evaluation, the position of carbonyl peak was monitored for 5,5-dimethylhydantoin (figure A-1), polymer **3** (figure A-2), and the reaction product (figure A-3). All of these compounds had C=O peaks in the $1715\text{--}1740\text{ cm}^{-1}$ region. The IR spectrum of the starting material for the DCM chlorination showed both ester (1736 cm^{-1}) and hydantoin (1718 cm^{-1})

signals. The IR spectrum of the reaction product remained mostly unchanged with peaks at 1734 cm^{-1} and 1715 cm^{-1} . It is unclear whether the conversion of the N-H bond into an N-Cl could be identified due to overlapping with the Boltorn carbonyl peaks.

In regard to the acetonitrile chlorination, the IR spectrum of the starting material (polymer **3**) only had one C=O peak displayed (figure A-4), which questions whether the hydantoin group was attached. However, the ^1H NMR (figure 8) clearly showed hydantoin and Boltorn peaks, so the absence of a second carbonyl peak in the IR spectrum was probably due to the overlapping of various C=O peaks. Similar to the chlorination reaction in DCM, the C=O peaks remained unchanged following the reaction (figure A-5). This observation pointed to possible peak overlap or the conclusion that the reaction was unsuccessful.

3.5 XPS Analysis of Chlorinated Hydantoin-Boltorn Films by TCCA Chlorination

Due to the inability to determine whether the chlorination was successful by ^1H NMR and IR, the reaction products were integrated into Estane films. XPS was used to determine whether the chlorination reactions were successful. XPS revealed minute amounts of Cl and F at the film surface, which indicated that the chlorination reactions were somewhat successful (table 3). The amount of fluorine at the surface was important because the purpose of the perfluorinated group was to promote self-segregation of the HBP to the surface. Therefore, a lack of fluorine indicated a low concentration of hydantoin-Boltorn H2O polymer at the film surface. All samples had a small amount of chlorine but the products obtained from reactions that were done in DCM (**AAW-3-68** and **AAW-3-95**) did not contain any fluorine; conversely, those products obtained from reactions that were done in acetonitrile (**AAW-3-52** and **AAW-3-93**) contained both chlorine and fluorine. Based on the low chlorine content found at the surfaces, TCCA chlorinations were not a viable option. These results indicated that DCM-TCCA chlorination reactions were unsuccessful, while acetonitrile-TCCA chlorinations were somewhat successful.

Table 3. XPS analysis of TCCA chlorinated hydantoin-Boltorn H2O Estane films.

Films	Atomic Concentrations %					
	C	F	Cl	N	O	Si
AAW-3-52	73.4	0.26	0.57	2.94	21.3	1.58
AAW-3-68	74.9	0.00	0.47	1.38	21.0	2.49
AAW-3-93	77.2	0.71	0.14	2.43	18.4	1.13
AAW-3-95	75.9	0.00	0.15	2.06	21.2	1.21

3.6 Chlorination of 5,5-Dimethylhydantoin Potassium Salt

In an effort to increase the chlorine content in the polymers, the sodium salt of 5,5-dimethylhydantoin was chlorinated with bleach (figure 13). If successful, this method would alleviate the need to chlorinate the polymer with TCCA or chlorinate films with bleach.

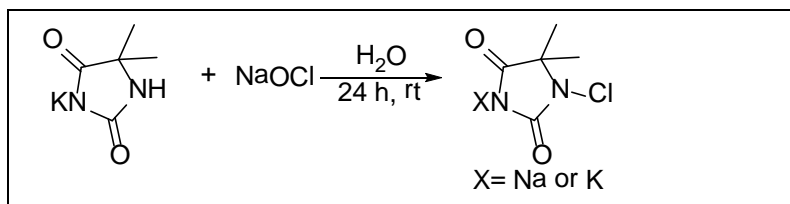


Figure 13. Chlorination of 5,5-dimethylhydantoin potassium salt.

3.6.1 Synthesis and Characterization of Chlorinated 5,5-Dimethylhydantoin Sodium Salt

The 5,5-dimethylhydantoin potassium salt (5.48 g, 32.9 mmol) was dissolved in water, followed by the addition of 23 mL of 13% bleach (2.94 g, 39.5 mmol). The reaction was stirred for 24 h, and then the reaction solution was concentrated with a rotary evaporator. A slight yellow solid was obtained.

The ¹H NMR of the product showed two methyl peaks (figure 14, Peaks A and B) and showed multiple peaks in the carbonyl ¹³C NMR region (figure 15, 160–200 ppm). These spectra suggested the possibility that two species were formed during the reaction (figure 16). The formation of the dichlorohydantoin salt (**6**) can be overcome because it would be nonreactive in subsequent S_N2 reactions, while the monochlorohydantoin salt (**5**) would remain reactive.

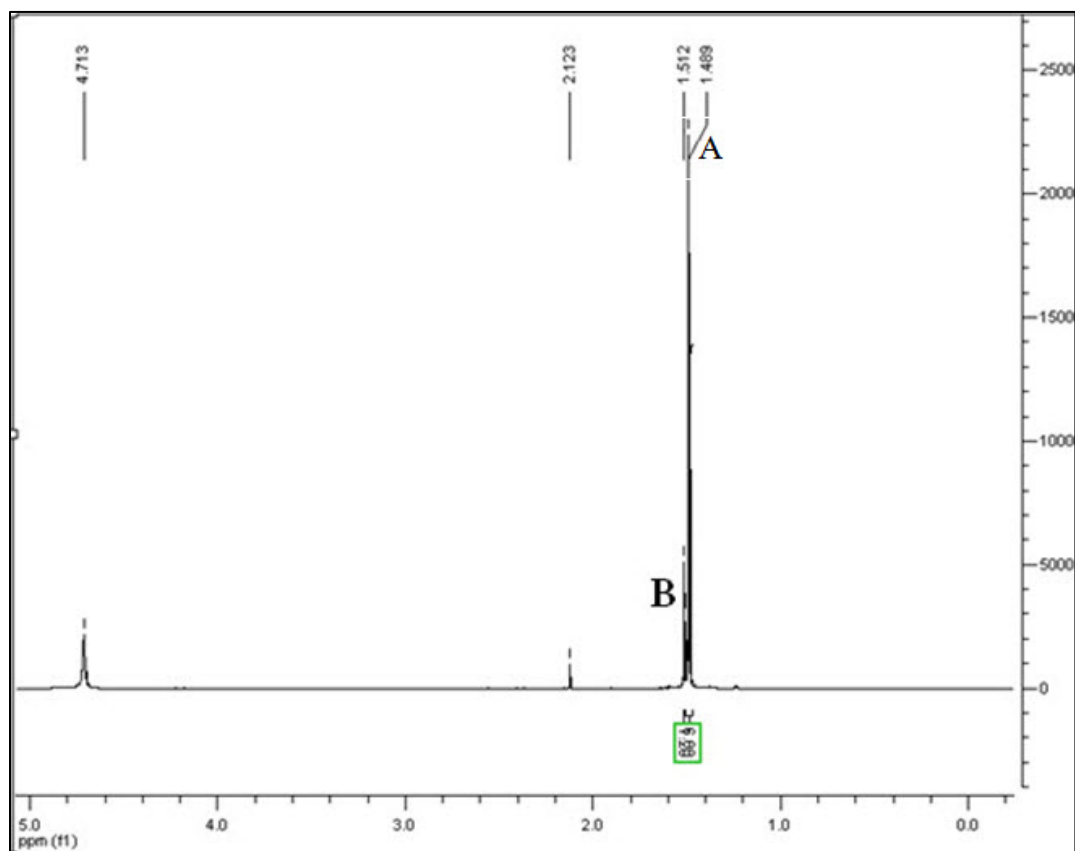


Figure 14. ¹H NMR spectrum for chlorination of 5,5-dimethylhydantoin potassium salt.

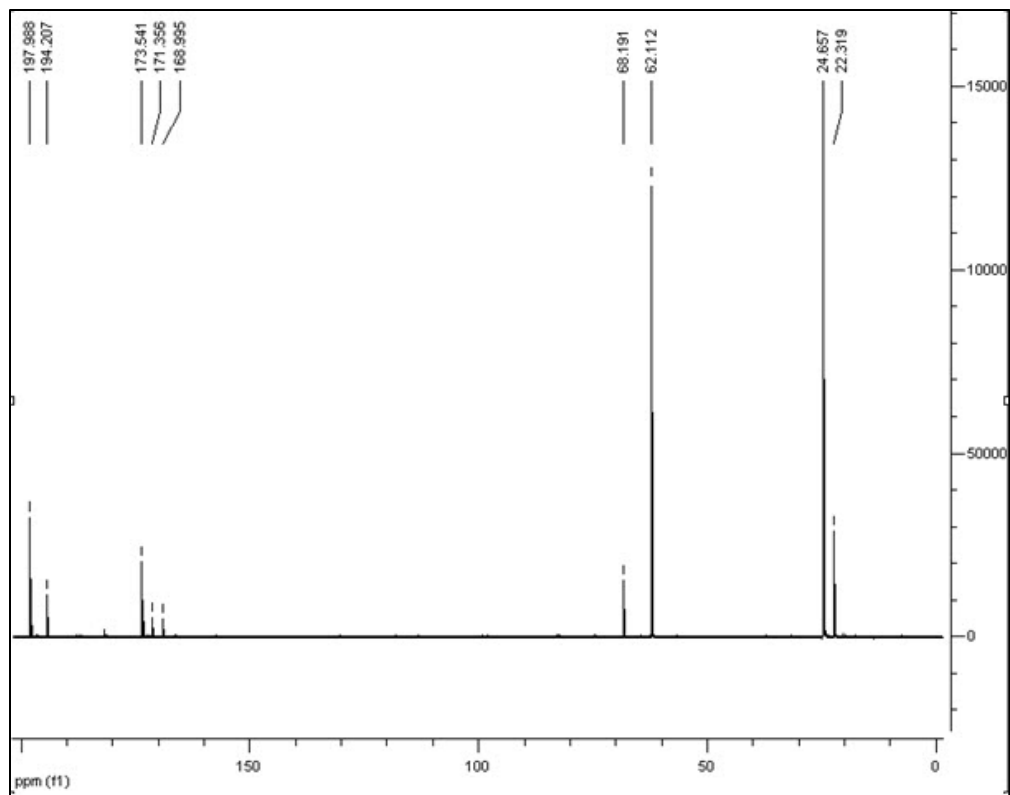


Figure 15. ^{13}C NMR spectrum for chlorination of 5,5-dimethylhydantoin salt potassium salt.

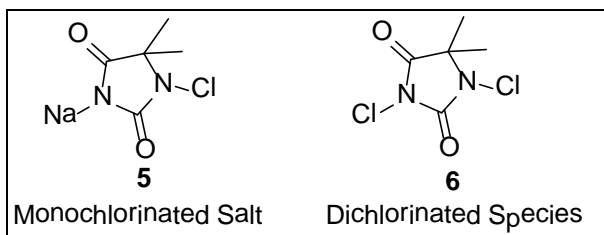


Figure 16. Possible chlorination products.

Two separate batches of chlorinated potassium salt were used in $\text{S}_{\text{N}}2$ reactions with polymer **2** (figure 17). Two reaction products (**AAW-3-130** and **AAW-3-131**) were incorporated into Estane films to evaluate the success of the chlorination of the 5,5-dimethylhydantoin potassium salt.

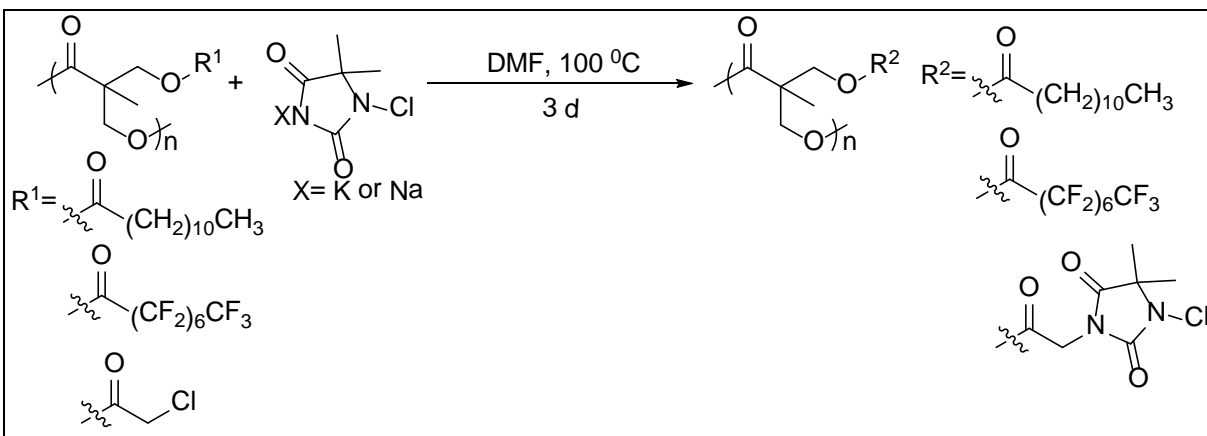


Figure 17. Formation of a prechlorinated hydantoin-Boltorn H20 polymer.

The reaction products were then integrated in Estane films and XPS was used to determine the chlorine content at the film surface (table 4). Samples **AAW-3-130** and **AAW-3-131** were made from the chlorinated sodium salt, while **AAW-3-99** was made from the nonchlorinated sodium salt. The results cast doubt whether the chlorination reactions were successful. Neither film containing **AAW-3-130** or **AAW-3-131** contained chlorine. However, both films did contain fluorine, which indicated that the HBP was present at the film surface. The presence of the HBP at the surface, combined with lack of chlorine, suggested that the chlorination of the 5,5-dimethylhydantoin potassium salt was unsuccessful.

Table 4. XPS analysis of prechlorinated hydantoin-Boltorn H20 Estane films.

Films	Atomic Concentrations %					
	C	F	Cl	N	O	Si
AAW-3-130	74.4	1.18	0.00	3.10	21.3	0.00
AAW-3-131	77.1	1.23	0.00	3.34	18.3	0.10
AAW-3-99	76.8	0.00	0.00	3.13	20.1	0.00
Estane Control	86.1	0.00	0.00	2.00	12.0	0.00

3.7 Iodometric Titration of Chlorinated Potassium Salt of 5,5-Dimethylhydantoin

In an attempt to explain the lack of chlorine in the 5,5-dimethylhydantoin potassium salt, iodometric titration was used to verify whether the potassium salt of 5,5-dimethylhydantoin was successfully chlorinated with bleach (figure 13). The bleach solution (13 %) used in the chlorination reactions was also evaluated.

Aqueous acetic acid solution was obtained after dilution from a 1 N stock solution. Aqueous sodium thiosulfate solution was obtained after dilution from a 0.1011 N stock solution. All dilutions were made using equation 1, where N=normality and V=volume. Potassium salt or bleach (0.5 g) was dissolved in a 0.1 N acetic acid solution. Potassium iodide (0.3 g) and aqueous starch (0.5%) was added to the acetic acid solution. The resulting solution was titrated

with sodium thiosulfate (0.0375 N) until the color of the solution was colorless. Starch was added to water and then heated with a heat gun to obtain a hazy white suspension.

$$N_1V_1=N_2V_2 \quad (1)$$

$$\% \text{Cl}^+=[N \times V \times 35.45/(2 \times W)] \times 100 \quad (2)$$

Oxidative chlorine percentage ($\text{Cl}^+\%$) was determined using equation 2. Symbols N, V, and W were normality, volume of the sodium thiosulfate consumed in the titration, and weight in grams of sample, respectively, and 35.45 was the molecular weight of chlorine.

In the literature (3), the starting solution should be blue and upon addition of sodium thiosulfate the solution turns colorless. However, these past literature reports were restricted to fibers. In these titration experiments, the initial color was orange. Upon addition of sodium thiosulfate, there was an instant blue color but the solution quickly went back to orange after the solution was swirled, then the color changed to green, and then turned “colorless” (endpoint).

The chlorinated sodium salt of 5,5-dimethylhydantoin was water soluble; therefore, no solubility issues were expected. Sodium thiosulfate turned the orange solution green after 2.5 mL. The solution turned colorless after a total of 4.5 mL of sodium thiosulfate was added. The endpoint was determined to be the point where the solution became colorless and the chlorine content was calculated to be 6%. This result indicates that the chlorination reaction did work to some degree. An optimized procedure for nonfibers was needed. The acetic acid used in these experiments probably reacted with the bleach and potassium salt, which could have altered results.

4. Conclusions

The synthesis of chloroamide-hyperbranched polymers was ultimately unsuccessful because of the inability to chlorinate the hydantoin group. Attachment of the hydantoin group was relatively easy but various chlorination methods either resulted in minor chlorination (TCCA) or no chlorination (bleach). The development of an alternative method that does not utilize TCCA or bleach chlorination would be beneficial; however, development of the hydantoin-Boltorn H20 polymer has ceased. Although the final reaction did not work, this project does demonstrate the ability of developing a HBP capable of self-segregation.

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Appendix. IR Spectra of Modified Boltorn Polymers

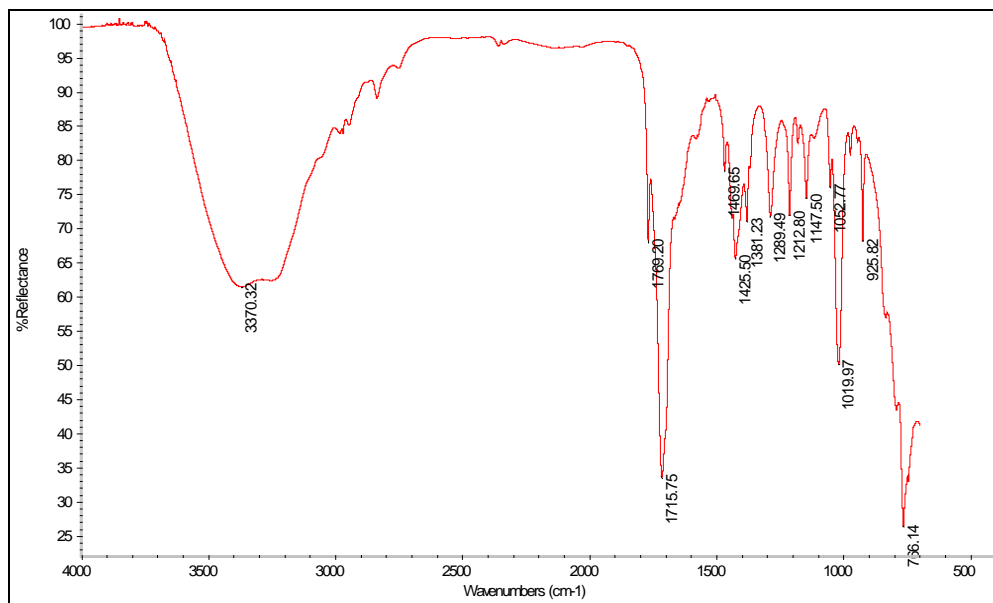


Figure A-1. IR spectrum of 5,5-dimethylhydantoin.

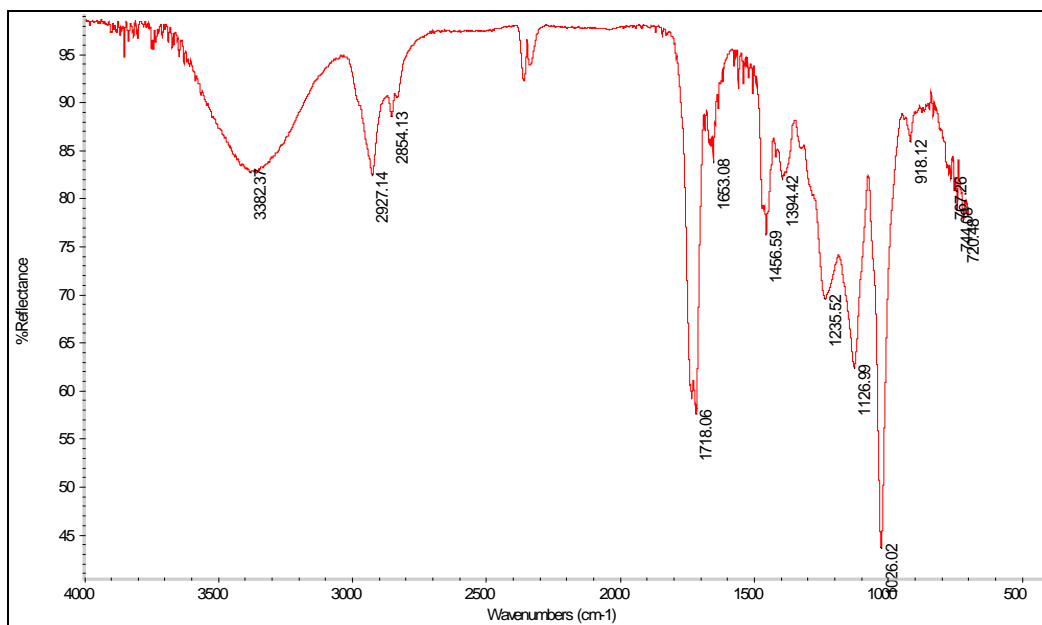


Figure A-2. IR spectrum of polymer 3. Wavenumber for peak at 1736.21 cm⁻¹ put in manually.

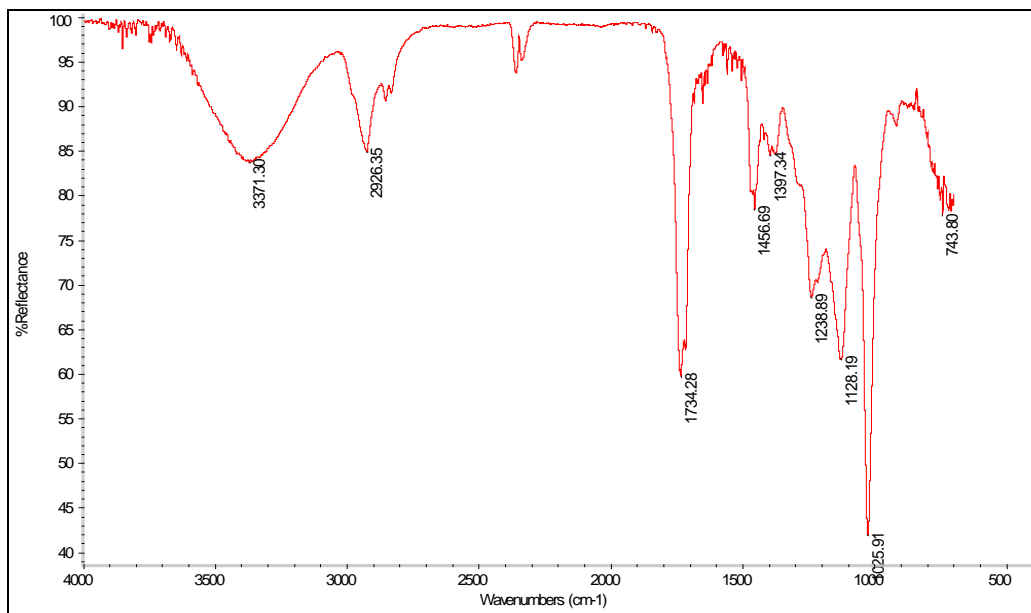


Figure A-3. IR spectrum of TCCA chlorination of polymer **3** in DCM. Wavenumber for peak at 1715.77 cm⁻¹ put in manually.

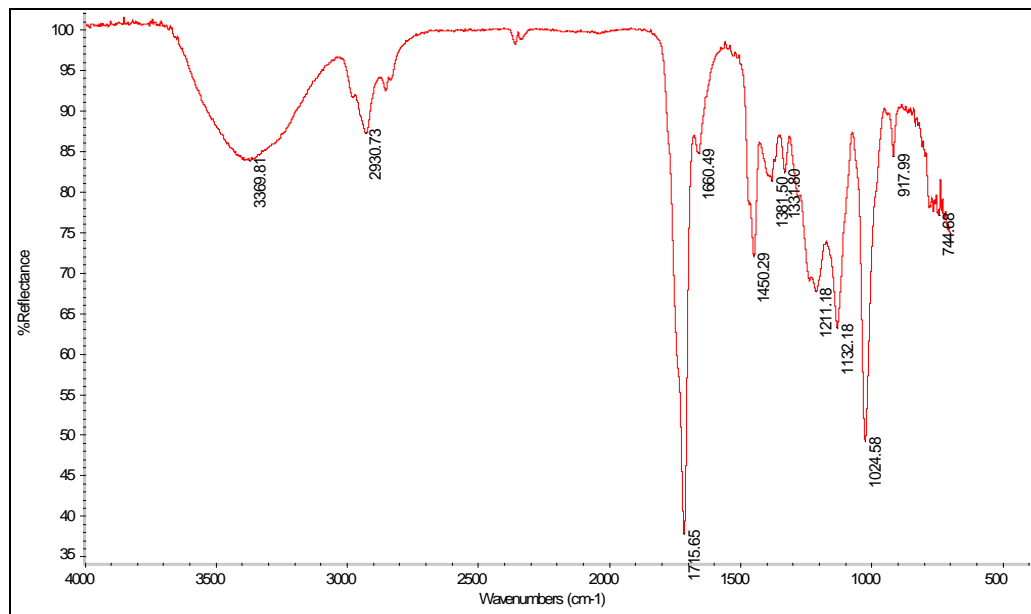


Figure A-4. IR spectrum of polymer **3** for acetonitrile chlorination.

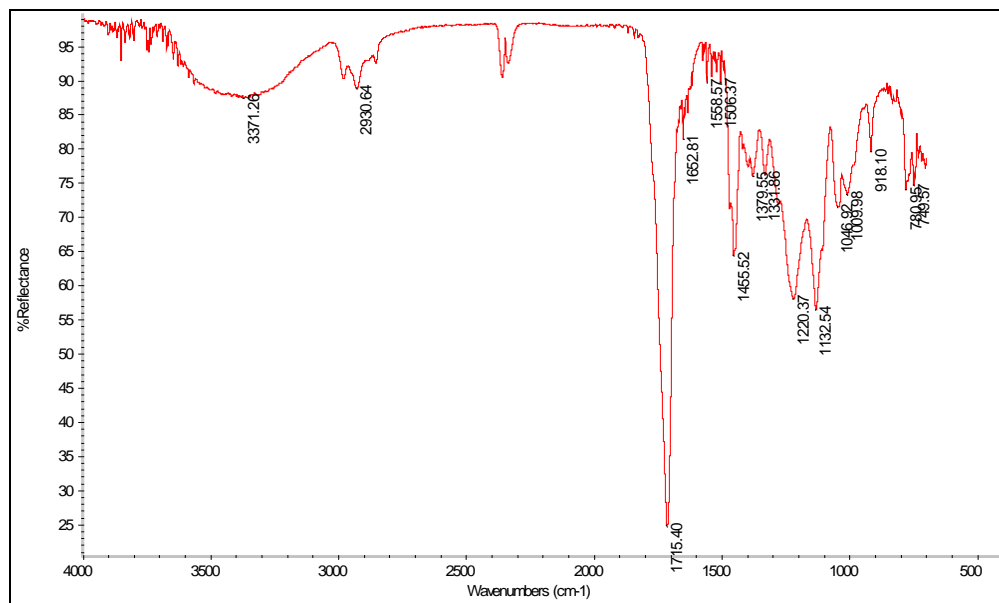


Figure A-5. IR spectrum of TCCA chlorination of polymer **3** in acetonitrile.

List of Symbols Abbreviations, and Acronyms

^{13}C NMR	carbon 13 NMR
^1H NMR	proton NMR
CDCl_3	deuteriochloroform
Cl^+	oxidative chlorine
DCM	dichloromethane
DMF	<i>N,N</i> -dimethylformamide
DMSO	dimethylsulfoxide
HBP	hyperbranched polymer
IPA	isopropyl alcohol
IR	infrared spectroscopy
N_2	nitrogen
Na_2SO_4	anhydrous sodium sulfate
NMP	1-methyl-2-pyrrolidinone
PFOA	perfluorinated octanoic acid
PMMA	poly(methyl methacrylate)
Ppm	part per million (chemical shift)
rt	room temperature
$\text{S}_{\text{N}}2$	bimolecular nucleophilic substitution
TCCA	trichloroisocyanuric acid
THF	tetrahydrofuran
VX	O-ethyl S-[2-(diisopropylamino)ethyl] methylphosphonothioate
XPS	x-ray photoelectron spectroscopy

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