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Creative Inquiry:

The process of exploring issues, objects, or works through the collection and analysis of evidence including combining or synthesizing existing ideas, products, or expertise in original ways to answer an open-ended question or achieve a desired goal.

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EDITORIAL

It is a time of change in Higher Education, and particularly here at Tennessee Technological University. The construction of the new Laboratory Science Building is the biggest physical change we see, but the process using of Creative Inquiry goes on behind the scenes, and is changing the way we teach classes and improve student learning. You may ask, how? Our new 5-year Strategic Plan incorporates creative inquiry within its very structure, even though it isn't specifically named as such, and addresses lack of diversity, encourages study abroad, and most importantly it actively fosters "experiential learning" which we know is within the scope of creative inquiry. It is certainly to the advantage of students and faculty to increase their appreciation of diverse ways of thinking and global learning to effectively increase critical and creative thinking as applied to problem solving. For more on TTU's Strategic Plan see:

<https://www.tntech.edu/strategic/>

Edward C. Lisic

Journal of Creative Inquiry

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South Korea Born Anew: The Korean Wave

Aaron Kahn

South Korea since times long past has seen years of chaos and destruction, first because of Japanese colonialism, then due to a civil war in the 1950s which prevented the nation from growing economically, socially, and culturally. As a result of the chaos brought on by this war, South Korea had to play “catch up” with the rest of the world in these areas. This “catch up” was accomplished by South Korea having an open-mind regarding imports and foreign cultural products. The Ancient Koreans adopted the Confucian values that still greatly influence Asian society to this day. In more recent years, Koreans adopted American lifestyles, Japanese modernity, and European philosophy.¹

During the Korean and Vietnam wars, soldiers brought back with them musical influences such as American rock and Japanese enka, as well as many more diverse musical styles. Local singers imitated these foreign musical styles creating a boom in the music industry and creating a miniature Korean Wave, an event South Korea had never experienced. This upsurge in the

culture industry was short-lived, because in 1961, Park Chung Hee instigated what is known as the May 16th Military Coup, gaining control over the nation of South Korea. While South Korea would progress economically during Park’s presidency, the nation would regress culturally because of the actions taken not only by himself, but also his successor, Chun Doo Hwan.²

On May 16th, 1961 Park Chung Hee crossed the southern end of the Han River taking over the country and achieving his military revolution. In the first moments of his revolution, Park established an anti-corruption campaign targeted towards the banking and business industries. Many businessmen were coerced into establishing businesses in designated industries to avoid any repercussions, but those in the banking industry were not given this opportunity. This anti-corruption campaign was the beginning of his many different plans to revitalize the South Korean economy.³

In 1962, Park enacted a five-year plan to revitalize the economy in which exportation

¹ Korean Culture and Information Service. “The Korean Wave: A New Pop Culture Phenomenon.” Contemporary Korea No.1. “Korean Culture and Information Service, Ministry of Culture, Sports and Tourism.” [file:///C:/Users/Aaron%20Khan/Downloads/KOREAN_WAVE_20110907%20\(8\).pdf](file:///C:/Users/Aaron%20Khan/Downloads/KOREAN_WAVE_20110907%20(8).pdf). accessed Nov 18, 2017 pgs. 17-18

² Ibid., Korean. pgs. 17-18

³ Breen, Michael. Park Chung Hee’s military coup and rise of military regime. The Korea Times.

http://www.koreatimes.co.kr/www/news/nation/2010/05/117_65949.html. Accessed Oct 3, 2017.

was the primary goal. To meet the amount of exportation necessary, various industries were given exportation targets, and if those requirements were met, they were given special treatment, tax benefits, and support from government bureaucrats. If these quotas were not met, companies throughout the nation would face threats of takeover by the government.⁴To eliminate any objections citizens may have with this policy, Park utilized the military to suppress any protests. With military force, Park utilized the limited amount of resources available to him to steer the country into economic stability.

On Oct 12, 1972, the establishment of the Yushin Regime Park accelerated his drive to stimulate the economy with the Saemaul Undong or New Village Movement. The goal of this program was to modernize agriculture and raise rural living standards. The New Village Movement began when over thirty-three thousand of the nation's villages were provided with 335 bags of cement, a half ton of iron rods, and a plan for what these materials were for.⁵

The New Village Movement consisted of four steps: the first was the gathering of the community and money; the second involved meetings among the various villages to convince the citizens that the New Village

Movement would be beneficial to the country; the third and fourth steps involved modernizing homes, establishing cultural facilities, and initiating cooperation between neighboring towns. Within nine years of the establishment of this program, the average rural income rose from just over two-hundred thousand won to over a million won. Rural poverty decreased and women gained a prominent place in their local governments.⁶

Despite the many successes that the Yushin Regime brought forth, it was an oppressive nightmare for the citizens of South Korea. Park established the Yushin Regime to accomplish his goals for the country in the shortest time possible with minimal opposition and maximum effectiveness. Using the monolithic control he gave himself in 1972, Park uncompromisingly monitored the government, bureaucracy, businesses, and citizens. Park also closely monitored all Korean citizens through agencies like the Korean Central Intelligence Agency or KCIA. Under the KCIA, Park Chung Hee maintained a system of checks and balances so strict that even families could not trust one another for fear of violence and retribution.⁷ Under the power of the Yushin Regime, Park imposed almost complete monolithic control over all

⁴ Ibid, Park Chung Hee

⁵ Ibid, Park Chung Hee and The Borgen Project. South Korea's New Village Movement. <https://borgenproject.org/new-village-movement-korea/>. Accessed Nov 18, 2017.

⁶ Ibid, The Borgen Project

⁷ Kim, Hyung-ah. "Korea's Development Under Park Chung Hee: Rapid Industrialization, 1961-79. London: Routledge. Rutledge Curzon/ Asian Studies Association of Australia (ASAA) East Asia Series. Vol 5. <http://search.ebscohost.com/login.aspx?direct=true&db=nlebk&AN=116099&site=ehost-live>. Accessed Nov 18, 2017. Part IV Conclusion.

aspects of life, both governmental and non-governmental. The army, chaebol, students, unions, and the young and old alike were under the control of Park.⁸

Park's political strategy centered around a guided democracy and state corporatism which resulted in both civilian and political life being heavily regulated for the sake of efficiency. Civilian society was reorganized under the military ideals of order, discipline, and collectivism. Every aspect of a citizen's life was under control of the rigidity and discipline Park readily believed in.⁹

Park Chung Hee's May 16th Military Coup was a revolution for national salvation and reconstruction to save the country from collapse by the socio-political and economic chaos the nation was in. To accomplish this national salvation, Park emphasized the importance of the nation rather than the individual. As stated by Park in this quote, "We should concentrate all our energy on eliminating old evils, thereby promoting 'national morality' and national spirit, improving national life in social, economic, and all other fields, thereby blocking

⁸ Kim, Hyung-ah. *Reassessing the Park Chung Hee Era, 1961-1979: Development, Political Thought, Democracy, and Cultural Influence*. Center for Korea Studies Publications. Seattle: University of Washington, 2011.
<http://search.ebscohost.com/login.aspx?direct=true&db=nlebk&AN=414393&site=ehost-live>. Accessed Nov 18, 2017. Part I Development.

⁹ Kim, Young-Ha. "The Park Chung Hee Era." *Part Two Politics*. pgs.115-116. Cambridge, Mass: Harvard University Press, 2011.
<http://search.ebscohost.com/login.aspx?direct=true&db=nlebk&AN=366637&site=ehost-live>.

Communist attempts at aggression and constructing a genuine welfare state."¹⁰

The goal of Park's military revolution can be summarized in the following quote. "The goal of the revolution is to weed out corruption, strengthen the autonomous ability of the people, and establish social justice... Therefore, democracy should be established by administrative means, not by political means, during the transition period." The transition period Park spoke of was the time between his coup in 1961 and the next presidential elections in 1963. Park was to allow democratic elections but elected himself president repeatedly over the years of his presidency against the consent of the citizens.¹¹

The many years of oppression that the nation of South Korea had suffered from under the rule of Park Chung Hee ended in 1979 when Park was assassinated by KCIA director Kim Jae-Kyu. Park Chung Hee's assassination brought peace to the citizens of South Korea, as his oppressive and violent rule was no more. Interim-President Choi Kyu-Hah's leadership was respected and

¹⁰ Ibid, *Reassessing the Park Chung Hee Era. Part Two Political Thought, Democracy and Labor* and Kim, Hyung-ah. "Korea's Development Under Park Chung Hee: Rapid Industrialization, 1961-79. London: Routledge. *Rutledge Curzon/Asian Studies Association of Australia (ASAA) East Asia Series. Vol 5.*
<http://search.ebscohost.com/login.aspx?direct=true&db=nlebk&AN=116099&site=ehost-live>. Accessed Nov 18, 2017. Part IV Conclusion.

¹¹ Ibid, Park Chung Hee

unchallenged. Students went back to school, the civil rights of rebels who opposed Park were reinstated, the South Korean Constitution was rewritten, and the “Seoul Spring” was set in motion. Unfortunately, the peace of the Seoul Spring would not last, because in April of 1979, Chun Doo Hwan appointed himself head of the KCIA and political protest began.¹²

On May 17, 1980, just one day after Park Chung Hee staged his own coup nineteen years earlier, Chun Doo Hwan announced that he was taking control over the country. Political activity was banned, politicians were arrested, universities were closed, and the media was censored. In response to the protests that arose with his ascent to the presidency, Chun deployed troops to the city of Gwangju to suppress student protests at Chonnam and Chosun Universities.¹³ One of the most well-known and tragic rebellions in South Korean history, the Gwangju Uprising, would soon take place.

From May 18 to May 27, citizens of Gwangju protesting martial law and Chun’s leadership became the symbols of South Korea’s fight for democracy. Protestors were beaten by military forces, flamethrowers were aimed at those who

appeared to be of college age, and hospitals began to quickly fill up with the dead and injured. The citizens of Gwangju gained an upper hand against the military when they drove them out of the city until May 27, when the military overran the city. At the end of this conflict, over two-hundred men, women, and children were killed.¹⁴

Chun Doo Hwan, unlike Park Chung Hee, often used less violent ways to oppress society. Chun instituted what is known as the 3S, or Sex, Screen, and Sports policy to control and appease society. In 1981, Chun began to promote baseball as a national sport as the first step in his 3S policy. Chun also used sex to manipulate the citizens by relaxing the strict moral codes placed on the society by Park Chung Hee, such as women wearing mini-skirts and the length of men’s hair. The citizens of Korea were now free from the curfew restrictions that had been in place and were free to enjoy the night-life as much as they wished. Citizens were encouraged to enjoy the “pleasure industry”, and entertainment buildings such as movie theaters were erected, the sole purpose of which was to show erotic films. Citizens were given some freedoms in the hopes that they would bend to his will.¹⁵

¹² Breen, Michael. General Chun Doo hwan took power in a coup. The Korea Times. http://www.koreatimes.co.kr/www/news/nation/2010/05/117_66347.html. Accessed Nov 18, 2017.

¹³ Ibid, General Chun Doo hwan

¹⁴ Ibid, General Chun Doo hwan and Kingston, Jeff. “Dying for Democracy: 1980 Gwangju uprising transformed South Korea,”. The Japan Times. <https://www.japantimes.co.jp/news/2014/05/17/asia-pacific/politics-diplomacy-asia-pacific/dying->

[democracy-1980-gwangju-uprising-transformed-south-korea/#.WiqhXUqnG00](https://www.japantimes.co.jp/news/2014/05/17/asia-pacific/politics-diplomacy-asia-pacific/dying-democracy-1980-gwangju-uprising-transformed-south-korea/#.WiqhXUqnG00).

¹⁵ Lee, Yun-Jong. “Woman in Ethnocultural Peril: South Korean Nationalist Erotic Films of the 1980s”. The Journal of Korean Studies. Vol. 21, Number 1, (Spring 2016) <https://books.google.com/books?id=CqRBDAAAQBAJ&pg=PA101&lpg=PA101&dq=lee+yun+jong+women+in+ethnocultural+peril&source=bl&ots=HAEUfalZqE&sig=5g9qP5pYfu9jOFowVMWrWp805DI&hl=en&>

Because of their violent and oppressive natures, the presidencies of Park Chung Hee and Chun Doo did not allow the nation to progress any further culturally than the levels from the Korean Wave of early 1950s. Priority during both Park and Chun's rule was to bring the country up economically as much as possible, and this was often accomplished through violence to bend society to their respective wills. Influences from foreign nations were deemed unnecessary, and as such, the arts were heavily regulated.

The movie industry more-so than others was censored as movie directors had to ensure they did not make anything of a political or sexual nature. Many directors during Park Chung Hee's time solely directed historical works, as they were the least controversial topic available to them. Foreign movies brought into the country were heavily regulated as well, because only Korean companies could distribute them and were put under the same scrutiny as Korean films.¹⁶

Democracy was achieved when Roh Tae-woo was elected president in February of 1988 marking the end of the authoritarian rule the nation of Korea had been under for twenty-four years. South Korea could now flourish both democratically and culturally, and it was at this time that Korean pop

culture started to become the cultural powerhouse it is now.¹⁷

Researchers such as Toru Hanaki from Nanzan University and Sang Yeon Sung from the University of Vienna believe that cultural proximity plays a significant role in why Korean pop culture has become so popular throughout Asia. South Korea is culturally and socially similar to countries like Japan and China where the Korean Wave first began.¹⁸

Cho Hae Joang, professor emeritus of sociology and cultural anthropology at Yonsei University, argues that the reason Korean pop culture became popular is because of the strong anti-Japanese and western sentiments that are prevalent in much of Asia. Additionally, South Korea has never invaded a foreign country unlike the Japanese or Americans, and thus, no negative feelings are harbored against South Korea. South Korea does not pose a threat, and as result, Korean cultural products are preferred. Many researchers, myself included, are also of the thought that government influences played the biggest role in the growth of the Korean popular culture industry. Scholars of this way of thinking focus on the government's role in shaping of the movie and broadcasting industries and the economic, political, and

[a=X&ved=0ahUKEwjP-cXw5svXAhUI2SYKHYZmDYUQ6AEINzAE#v=onepage&q&f=false](http://hdl.handle.net/1887/20142). Accessed Nov 18, 2017. and Tuk, William. "The Korean Wave: Who are behind the success of Korean popular culture?" Leiden University Repository. <http://hdl.handle.net/1887/20142>. pg. 7

¹⁶ Ibid, Tuk, William, Pgs.8-9

¹⁷ "Transition to a Democracy and Transformation into an Economic Powerhouse". Korea.net. <http://www.korea.net/AboutKorea/History/Transition-Democracy-Transformation-Economic-Powerhouse>. accessed Nov 18,2017.

¹⁸ Ibid, Tuk, William, pgs.3-4

commercial aspects that led to the success of Korean pop culture as well.¹⁹

One final area of research commonly used to explain the popularity of Korean pop culture is the concept of “hybrid culture”. I believe this, in combination with government influences, played a significant role in evolution of the popularity of Korean pop culture. “Hybrid culture”, or hybridity, is a term coined by Doo-bo Shim, a professor at Sungshin Women’s University. Many see Korean pop culture as a hybrid culture of its own or as a mixture of both eastern and western influences. Cultural products are modified to appeal to Asian consumers as well as western audiences. Korean dramas and music are a mixture of both the familiar and exotic while still retaining what makes them Korean.²⁰

Alongside these areas of research there are five additional factors that are believed to have contributed to the success and evolution of the Korean Wave. In the early 1990s, a ban on foreign travel enacted by Park was lifted, and the nation of Korea began to explore the cultures of the U.S. and Europe when previously western influences had been shunned. Many college students began to attend foreign universities, and when they returned home they brought with them new ideas about business and new perspectives on the arts and other forms of expression.²¹

¹⁹ Ibid, Tuk, William. pg. 4

²⁰ Ibid, Tuk, William. pgs.3-5

²¹ “Korean Wave (Hallyu)- The Rise of Korea’s Cultural Economy & Pop Culture. Martin Roll:

At the time of the restructuring of the chaebol in 1997, South Korea was undergoing a financial crisis much like the rest of Asia, and the chaebol were key in bringing South Korea out of an economic crisis. The chaebols consisted of business conglomerates that operated in every sector of the economy, and the economic crisis forced these businesses to restructure the very way they operated. They began to focus solely on their core competencies allowing for more entrepreneurs to emerge and stimulate the economy. The nation of South Korea realized that their economy relied too much on the chaebols and that if they failed the South Korean economy would fail in the process. Kim Dae-Jung, president at the time, pushed for the expansion of the technology and cultural industries to industrialize the nation and reduce reliance on the chaebol. As South Korea became industrialized, the pop culture industry became their most important cultural export which changed how South Korea was viewed by the rest of the world.²²

In 1996, the censorship laws of the previous generation were abolished, and filmmakers and artists alike were free to express themselves in whatever way they saw fit. Artists of all kinds now had open to them genres and styles of music never available to

Business & Brand Leadership.
<https://martinroll.com/resources/articles/asia/korean-n-wave-hallyu-the-rise-of-koreas-cultural-economy-pop-culture/>. Accessed Nov 18, 2017.

²² Ibid, Korean Wave (Hallyu)

them before, and they began to experiment with these styles and never looked back.²³

Major Korean chaebols in the mid-1990s began to focus on the quality, design, and branding of their products on a global scale. The focused attention on the overall quality of goods began to leak into other industries, and soon it was standard to provide the global market with the best possible goods. The final factor that contributed to the mass the popularity of Korean pop culture is the increased focus on South Korea's infrastructure, specifically that of the entertainment and technological fields. In 2012, government funds made up twenty-five percent of all venture capital money disbursed in South Korea, one-third of which was spent on the entertainment industry²⁴

In June of 1997, a new culture, the Korean Wave, was born in China when the Korean drama *What is Love* aired on national television. *What is Love* depicted familial tensions between a husband and wife, one of which has a family that is conservatively minded and the latter liberally minded. The Chinese were enthralled with the free-spirited attitudes of Korean life they saw in this drama that they had never experienced under socialism in China. The Chinese could also relate more to Korean dramas rather than those from America as they were centered around Confucian family values rather the individualistic attitudes prevalent

²³ Ibid, Korean Wave (Hallyu)

²⁴ Ibid., Korean Wave

²⁵ Ibid., Korean, pgs. 20-21

in American television. At the height of its popularity, *What is Love* achieved the second highest ratings ever at the time for a foreign television program in China at a fifteen percent audience share. Korean dramas from this point on grew in popularity and spread to other regions in Asia.²⁵

In 2003, Korean dramas spread to Japan with the program *Winter Sonata*. This drama told the story of a man and woman tied together by fate and was met with resounding success. *Winter Sonata* elicited a significant response from middle-aged Japanese women creating the world's first Hallyu or Korean Wave stars Bae Yong-Joon and Choi Ji Woo. Bae Yong-Joon grew so popular that he gained the name Yon-sama, a name denoting much respect. On a visit to Japan in 2004, nearly five thousand women rushed to Haneda Airport in Tokyo to greet Bae upon his arrival. Bae's popularity grew so large in Japan and penetrated society so deeply it became known as the Yon-sama Social Phenomenon. When an episode of *Winter Sonata* was canceled to televise the Japanese Prime Minister's visit to North Korea, NHK, the television channel airing *Winter Sonata*, received over three-thousand phone calls in protest.²⁶

The Korean Wave reached the global world with the drama *Daejangeum* or *Jewel in the Palace*. This drama is based on the true story of an orphaned girl becoming

²⁶Ibid., Korean, pgs.23-25

physician to the king of Joseon. *Jewel in the Palace*, keeping with popularity of Korean dramas at the time, achieved the highest ratings ever for a drama at a fifty-seven percent audience share. Many people for the first time were experiencing the elegant dress and architecture of Korean royalty and the Joseon dynasty. China and Japan became enamored with both traditional and modern Korean culture.²⁷

Never has the popular culture of a country united the world as much as the cultural industry of South Korea. Under the rule of Park Chung Hee, the citizens of South Korea suffered under the oppressiveness of his Yushin Regime and a total lack of control over their own lives. Under Chun Doo Hwan, the citizens began to see more freedom because of his 3S policy, but he often resorted to violence as his rule was seen as illegitimate by many. When democracy was ushered in with the fall of Chun Doo Hwan, the Korean Wave emerged with the freedom of its nation, and since that day, South Korea was born anew.

Many question why Korean pop culture has become so popular throughout the world, and much research has been done to find this reason. From Doo-bo Shim's cultural hybridity to Cho Hae Joang's cultural proximity, opinions differ greatly, but one thing is universally agreed upon: the Korean popular culture industry is a cultural phenomenon that transcends hemispheres.

The success of the Korean pop culture industry cannot solely be attributed to the immense popularity of its television dramas but its music industry as well. In the early 2000s, K-pop idols BoA and Rain emerged, forever changing the Korean music industry. BoA, or the Queen of Korean Pop as Kwon Bo-Ah is known, is one of the very first Korean singers that could be considered globally popular. Throughout her career, BoA has catered her music towards her foreign fan base, and as a result became extremely popular in Japan. She became the first foreign artist ever to reach number one on the Japanese Oricon weekly album chart seven times.²⁸

Jung Ji-Hoon, or as he is better known, Rain, is one of the most successful male Korean singers and actors of his time. Jung Ji-Hoon is a model, actor, and singer whose career spans seven albums, six of which are in Korean and one of which is in Japanese. His acting career began in 2003 with the television drama *Sang Doo! Let's Go to School* in which he plays the love interest of actress Gong Hyo-Jin.²⁹

The cultural industry of South Korea evolved significantly with the emergence of what is known as the third generation of K-pop. Beginning in 2010, because of the internet and social media, the Korean Wave spread across the world with a speed and intensity much faster than at its inception. This was the birth of the Neo-Korean Wave,

²⁷Ibid., Korean, pg.27

²⁸ Ibid., Korean, pgs.31-32

²⁹ Ibid., Korean, pg.33

and the internet allowed for nearly universal access to Korean dramas and music.³⁰

Many Korean entertainment companies, especially those who comprise what are known as the Big 3, have utilized social media and video sharing websites such as YouTube to garner a larger fan base for their artists. Girls' Generation, an idol group part of the company SM Entertainment, has reached over forty-two million views on just one of their music videos uploaded to YouTube.³¹ One of the world's most widely used services has allowed this video and K-pop to prosper and bring people of multiple different cultures together.

References

Breen, Michael, "Gen. Park Chung Hee's May 16 Coup and rise of military regime," *The Korea Times*, May 16, 2010, accessed Oct 3, 2017.

Breen, Michael, "General Chun Doo Hwan took power in a coup." *The Korea Times*, May 23, 2010, accessed Nov 18, 2017.

Kim, Hyung-ah and Clark W. Sorenson. Edited. *Reassessing the Park Chung Hee Era, 1961-1979: Development, Political Thought, and Cultural Influence*. eBook. Seattle: Center for Korea Studies. University of Washington. 2011. accessed November 11, 2017.

Kim, Hyung-ah. *Korea's Development Under Park Chung Hee: Rapid Industrialization, 1961-79*. eBook. London: Routledge. 2004. Accessed November 11, 2017.

Kim, Young-ha. *The Park Chung Hee Era: The Transformation of South Korea*. ed. Byung-kook Kim and Ezra F. Vogel. eBook. Cambridge Mass: Harvard University Press, 2011. Accessed November 11, 2017.

Kingston, Jeff, "Dying for Democracy: 1980 Gwangju uprising transformed South Korea," *The Japan Times*, May 17, 2014, accessed Oct 3., 2017,

Korean Culture and Information Service. "The Korean Wave: A New Pop Culture Phenomenon." PDF. Korean Culture and Information Service. Nov 25, 2011. Accessed Nov 6, 2017.

Lee, Yun-Jong, "Woman in Ethnocultural Peril: South Korean Nationalist Erotic Films of the 1980s." *The Journal of Korean Studies* Volume 21, Number 1 (Spring 2016) accessed Oct 28, 2017.

Martin Roll: *Business & Brand Leadership*, April 2017, accessed Oct 28, 2017, <https://martinroll.com/resources/articles/asia/korean-wave-hallyu-the-rise-of-koreas-cultural-economy-pop-culture/>.

"South Korea's New Village Movement." *The Borgen Project*. Dec 20, 2015. Accessed Nov 18, 2017. <https://borgenproject.org/new-village-movement-korea/>.

Tuk, William, "The Korean Wave: Who are behind the success of Korean popular culture?," master thesis, Leiden University, accessed Oct 28, 2017.

³⁰ Ibid., Korean, pg.38

³¹ Ibid, Korean, pg. 47

Gang Violence and Homans' Social Exchange Theory

Presley H. Alford

The violence associated with gang counterculture is incredibly detrimental to the American value system. Gangs are comprised of a unique counterculture that both promotes and prioritizes violence. A gang is formally defined as, "a group of three or more persons with a shared goal, and sometimes common clothing identifiers and symbols, engaged in criminal activity for the advancement of their gang"(Schmidt & O'Reilly 2007). While conformist ideology promotes mores, laws, and norms, gang counterculture promotes deviance, lawlessness, and criminality. The gang value system awards power and prestige for acts of violence. By rewarding deviance, gang members are encouraged to continue engaging in violent behaviors, therefore encouraging gang members to seek to achieve status both within their own gang and among other gangs through criminality. Based on the Bureau of Justice Statistics, "on average for each year, gang members committed about 373,000 of the 6.6 million violent victimizations"(Harrell 2005). While this may appear insignificant, gang violence is difficult to measure as it falls subject to the dark figure of crime. Gang counterculture teaches members that the punishment for cooperating with law enforcement is far worse than a jail sentence. Thus, gang violence is far more common than statistically evident.

George Homans developed Social Exchange Theory in 1958 as a means to examine the

effects of costs and rewards on behavioral modification. Social Exchange Theory explains the relationship between consequences and future actions. Homans theorized that costs and rewards determined whether an individual would continue to engage in a specific behavior. Costs and rewards modify behaviors through operant conditioning. Homans explains in his research, "the behavior has been reinforced and undergone operant conditioning"(Homans 1958). Homans also focused on how reaction affected future behavior. Social Exchange Theory describes the factors that modify future behavior and the rate at which this was accomplished. Homans goes on to explain, "he [learning theorists] is interested in what determines changes in the rate of emissions of learned behavior"(Homans 1958). The reaction modifies future behavior through a process of positive, negative, or neutral consequences. Homans' theory has six basic propositions which include: success, stimulus, value, deprivation-satiation, aggression-approval, and rationality. Each proposition focuses on a different aspect of behavioral reinforcement. Thus, Homans' Social Exchange Theory explains the way in which future behavior is modified through the consequences outlined in his six basic propositions.

Homans Social Exchange Theory is applicable to the counterculture of violence that exists within gangs. Gangs engage in

violence in order to achieve status among other gangs, as well as to improve their own ranking within their own gang. Achieving such power and prestige serves as a reward for their violent and destructive behaviors. Homans' success proposition correlates with this display of behavior by gangs. Ritzer and Stepnisky define the success proposition as, "the more often a person is rewarded for a particular action, the more likely the person is to perform the rewarded action" (Ritzer & Stepnisky 2013). Gang members receive gratification for their acts of violence through both status in the hierarchy system as well as prestige among other gangs. The more frequently gang members are rewarded for their harmful behaviors, the more they will continue to engage in violence. The structure of the hierarchy system encourages destructive behavior through the means of costs and rewards. Schmidt and O'Reilly explain,

many of the national gangs have a structured organization. These gangs can be highly or loosely structured. The larger the gang, the more likely it is to be highly structured. For example, major Chicago gangs are highly structured with literature or "lit books" that describe the gang's history, leadership, rules, alphabets, codes and symbols, prayers and poetry, violations and consequences for committing a certain number of violations. Some national gangs have gone so far as to create their own constitution and by-laws. There are some gangs with one national leader and other gangs with set or clique leaders

Thus, gang members are rewarded for enacting violence, yet experience a cost effect if they disobey the code of the gang. The consequences associated with the member's decision to comply with violence or disobey with conformity, modifies their future behavior. Therefore, the more often gang members are rewarded with power and prestige, the more likely they are to act violently in the future.

The hierarchy that exists within gangs acts as a behavioral reinforcer. Gang members must succumb to the structured counterculture of the gang in order to achieve status. Gang members receive costly punishments, often in the form of physical abuse or even death, for deviating from the established violent value systems. Homans' rationality proposition explains that when deciding between alternate actions, the individual will choose the action in which the value of the result has the greatest probability of getting the desired outcome (Ritzer & Stepnisky 2013). Simply stated, gang members have more respect for the code of the streets than formal legal sanctions and will, therefore, continue to engage in violence. Gangs only recognize one way to end membership: 'blood-in, blood-out' (National Gang Center 2018). Thus, members with higher rank can inflict death as a punishment for those who deviate from the established codes. Gang members rationalize criminality as a means of obtaining the more valued outcome. Gang members are conditioned to seek acceptance and avoid the costs of punishment in the form of status among their fellow members. By enacting violence, gang members are

rewarded with status, often in the form of a higher rank or sex. Schmidt and O'Reilly explain a specific occurrence in which a young initiate was told, "shoot him and you can have a high rank"(Schmidt & O'Reilly 2007). Gang members are initiated at incredibly young ages and are thus, far more susceptible to the influence of those with higher rank. Initiates learn to rationalize violent behavior as a means of survival in the violent gang counterculture. Initiates seek to quickly achieve status, through violence, as a means of protection. The higher the rank of the gang members, the less likely they are to receive physical punishments. Gang members do not view themselves as a part of traditional American society. Instead, gangs are completely immersed in the power, prestige, and profit associated with acting out violence. Thus, gangs are engaged in a counterculture, consumed with the costs and rewards enforced by the code of the street.

Gang counterculture is also applicable to the deprivation-satiation proposition outlined in Homans' Social Exchange Theory. Each member's display of violent behavior will result in a consequence for which there will be either a cost or a reward. However, the more gang members are rewarded or penalized for behavior, the less valuable consequences become (Ritzer & Stepnisky 2013). This often results in greater violence as a means to obtain the same excitement associated with deviance. Such patterns of conditioning result in behavioral modifications. Gang members will increase their violent activity as a means of achieving the same satisfaction associated with early

membership. Homans' stimulus proposition outlines the relationship between past behavioral reinforcers and likelihood of an individual responding to similar stimuli. Gang members realize they will either commit the violent act or be physically beaten for disobeying the code of the gang. Similarly, by engaging in violent acts, gang members are able to earn power and prestige within their gang, as well as among rival gangs. Violence serves to behaviorally modify the members of gangs, resulting in a culture that is uniquely responsive to deviance. Thus, by acting in a way that will result in an outcome that is appealing to the individual, the action is likely to be repeated. The actions of gang members also directly correlates to Homans' value proposition. Earning such power and prestige within the gang works to serve as a reward and, therefore, holds value. Gang members value their status within the streets and are, therefore, more inclined to enact violence. Homans' success proposition explains the way in which gang members repeat violent behaviors upon receiving rewards. Gang members, especially young initiates, view the gang as all consuming. Members lack the ability to relate to traditional American society and conformists ideology. Thus, upon receiving the rewards of status and rank within the gang, violent behavior is perpetuated. Gang members also seek status as a means of protection. Members are less likely to suffer physical abuse if they 'outrank' other gang members. Social Exchange Theory also uses environmental reaction to explain behavior modification. Gang members are completely intertwined within their counterculture, and

as a result, their environment is that of the gang. When the gang reacts positively, the behavior continues, and when the gang reacts negatively, the behavior stops. Homans' aggression-approval proposition explains that when an individual does not receive the expected consequences, they react with aggression, in turn adding value to the actions. Gang members, especially young initiates, seek to please those whom outrank them. Thus, when approval is not received, members react with aggression. However, when members do appease those in the higher ranks, they not only avoid physical abuse, but also typically receive rewards. Thus, gang members continue to enact violence due to their behavioral modifications. The counterculture that exists ensures that gang members have the value system which revolves around deviance, criminality, and violence. Gang members become submerged in a counterculture wrought with violence and perpetuated by costs and rewards.

Homans' Social Exchange Theory examines behavioral modification through the means of costs and rewards. Behaviors that are rewarded will become persistent, whereas behaviors that result in a cost will end. The principles of Homans' Social Exchange Theory enable social scientists to understand behavioral modifications. Society has numerous sanctions that reward conformity and punish deviance, therefore perpetuating conformist ideology. However, in the context of gang counterculture, internal sanctions promote deviance. Thus, Homans' Social Exchange Theory can be applied to large scale society in both the context of

deviance and conformity. Just as with conformity, when deviant behavior is rewarded, it persists. Within a gang environment, juveniles are rewarded for deviant acts, thus perpetuating criminality through the process of behavioral modification. Homans' Social Exchange Theory is applicable to research, as it enables social scientists to understand both conformists and deviant ideology and from where these behaviors stem.

References

- Criminal Justice and Gangs. (n.d.). Retrieved from National Gang Center website: <https://www.nationalgangcenter.gov/about/FAQ>
- Harrell, E. (2005, June). *Violence by Gang Members*. Retrieved from <https://www.bjs.gov/content/pub/pdf/vgm03.pdf>
- Homans, George C. "Social Behavior as Exchange." *American Journal of Sociology*, vol. 63, no. 6, 1958, pp. 597–606. JSTOR, www.jstor.org/stable/2772990.
- Ritzer, G., & Stepnisky, J. (n.d.). *Contemporary Sociological Theory and its Classical Roots*.
- Schmidt, L., & O'Reilly, J. (2007). *Gangs and Law Enforcement : A Guide for Dealing with Gang-Related Violence*. Springfield: Charles C Thomas Publisher.

Toxic Attitudes: Martineau's "Criticism on Women" and the Rhetoric of Shame

Kinsey B. Potter

Abstract

Martineau's view that patriarchal society limited women's status coincides with Wollstonecraft's observation of how female minds were dulled in a society that prohibited them education. Martineau also saw that women choose an obedient place over education. Contemporary studies of shame, like Merleau-Ponty's, which observe shame causes a woman to "lose ... [a] sense of reality" (165), explore shaming of women-- still a powerful tool in discrediting women. Both Martineau and Wollstonecraft demonstrated intrinsically in their works that society needed to be analyzed and perfected before women could achieve rights. Both expressed their vision of a better future for women, and the more liberated position of women today is undeniably due to them. Paradoxically, both writers underscore Kristeva's conclusion that shame can "preserve what existed in the archaism of pre-objectal relationship" and allow women to embrace their power as a *real* human being (15) by subverting patriarchal power structures.

Harriet Martineau saw the shaming of women, particularly the lack of education granted to them due to their gender, as possessing the potential to, as later formulated by the French theorist and feminist Julia Kristeva, "preserve what existed in the archaism of pre-objectal relationship," or the relationship of women and men based on their shared blood instead of societal termed differences, and allow women to embrace their power as a *real* human being by subverting patriarchal power structures (Kristeva 15). Martineau's view that patriarchal society limited women's status coincides with the views of other feminist writers during times of gender discrimination, particularly with Mary Wollstonecraft's observation of how female minds were dulled in a society that prohibited them education. However, unlike

other female writers at the time that wished to *change* society, Martineau found strength in the status quo—particularly the "sociocultural expectations" and "narrow interpretations of who women are 'supposed to be,' based on their identity ... and/or their role," which Brene Brown points out of course limit women (Brown 46). Martineau expressed her vision of a better future for women, emphasizing the necessity for society to be analyzed and perfected before women could achieve rights. Despite the illnesses she suffered and gender based discrimination she faced, Martineau succeeded in showing the women of her time the importance of embracing what shames them and transforming the experiences of their shame into the determination to be educated and viewed as equal to their male counterparts.

Undeniably, the more liberated position of women today is due to writers such as Martineau.

According to the Shame Resilience Theory based on experiments under Brene Brown, previously quoted, women experience shame “as a web of layered, conflicting, and competing expectations that are, at the core, products of rigid socio-cultural expectations” that are “often imposed, enforced, or expressed by individuals and groups” (46). Nick Fox, the professor of Sociology and the Body at the University of Sheffield, points out that from birth,

human bodies are shaped to fit into cultural norms and expectations, through to the acquisition of language and training in the cultural rules of a particular society ... The latter [women] extends from rules of politeness and decorum such as ‘table manners,’ modest behavior or respect for elders or authority [men], through to more detailed culture-specific knowledge and understanding (133).

These expectations act as “unwanted identities” that discourage women “from sharing opinions that might make others feel uncomfortable or taking an unpopular stand on an issue” (Brown 46). In Martineau’s time, the main “unwanted identity” was being masculinized, which demanded for an equal education to men, particularly because “the sum and substance of female education” was “training women to consider marriage as the sole object in life, and to pretend they don’t think so” (“Woman”). In

other words, an educated woman who could find strength in writing/gaining knowledge was potentially damaging her profession as a wife, which consequently shamed her for going against societal norms.

In addition to being discouraged to write/take advantage of education because of her gender based shame, Martineau also possessed the shame of illness, which Rachel Ablow, an English professor at the University of Buffalo, describes as consisting of “digestive difficulties, anxiety attacks, and a progressive hearing impairment” throughout her life (Ablow 677). She equated shame with pain, in her case quite literally, in which both entities have “the potential to be attached to new associations, experiences, or beliefs.” However, ultimately Martineau’s experience proves that a woman’s shame can become her strength; the experience of shame acts as the mountain she must be determined to climb to reach her self-liberty, thus consequently elevating her higher than her male counterparts. The “sufferer from pain,” or the woman facing the shame of her gender, can thus emerge “in her account as the ideal legislator, albeit one who is prohibited by her condition [of shame; for example, her gender or her illness] from acting in the world.” Martineau never sought to hide her illnesses, and many of her writings address “issues of sickness, health, and disability in explicitly personal terms,” causing the reader to assume that shame, in Martineau’s mind, is an illness in itself (Ablow 677).

In her article “Professor of Parody,” Martha Nussbaum explains the ideas of Judith

Butler, the author of *Gender Studies* which focuses on women's studies. According to Nussbaum, Butler's main idea was that "gender is a social artifice," in which the shame of one's gender "reflects nothing that exists eternally in nature" but instead "derive[s] from customs that embed social relations of power." In other words, the effects of shame, as well as shame itself, is "shaped by forces that are social rather than biological." However, in *Gender Trouble*, Butler paradoxically states that the biological body of the female "works along magical relations of reciprocity whereby the female sex becomes restricted to its body, and the male body, fully disavowed, becomes, paradoxically, the incorporeal instrument of an ostensibly radical freedom." So, like Martineau's physical illness which gave her shame, the female body itself is a cause of shame for the woman due to societal conceptions of the difference in men and women from birth. In fact, Mary Wollstonecraft was shamed for her reputation as possessing a bastard child and having relationships with men who were already married, such as the artist Henry Fuseli, which her widower shared with the world in a memoir after her death. Her infidelity was not uncommon during her time period, but the fact that she was physically a woman and was being unorthodox with her *body* created a shame that eventually tainted her reputation. If shame acts as an illness, then the body of the woman is the same as the ear was for Harriet Martineau: It created a barrier between the woman herself and the natural world around her. Just as Martineau struggled to hear, women struggled to be respected because

they were limited to such high societal standards revolving around housekeeping and child bearing. The body of the woman, as Butler pointed out, restricted her from the radical freedom that the body of a man gave to him, and similarly the ear of Martineau restricted her from the freedom of hearing. In her article "Harriet Martineau: Gender, Disability, and Liability," Sarah Bohrer points out that Martineau considered the main way to analyze "the cultural framework that determines the meaning of femininity" is through the "analysis of biological and anatomical structures," portraying the importance of the physical body of women to Martineau as being the initial cause of shame within her.

In her essay "Criticism on Women," Martineau praises Queen Victoria of England as one of the first women whose mistreatment represents the difficulties women in powerful positions face. Martineau points out that, just as she was granted deafness against her will, Queen Victoria was put into her powerful position "by no seeking of hers," carrying the weighty shame of her gender. Subsequently, the women of her time period were put into their expected places of housewife, mother, and caretaker by no choice of their own, ironically equalizing Queen Victoria's power with a common woman's duties—both were set in place by tradition and *society*, but unwanted by the woman herself. Therefore, just as it was cruel for the men surrounding Queen Victoria to mock her youth and womanhood with "curses on the laws which placed [her] ... in her powerful position," even comparing her to "Marie Antoinette, a glittering star which set in

blood,” it was equally cruel for men to mock the shame of a woman’s gender as being enough to stop her from gaining an education. Martineau states that “the man who reproaches her or insults her . . . is guilty of an immorality and a cruelty akin to his who scoffs the baldness of the old or the blindness of the blind,” or in Martineau’s case—the deafness of the deaf (“Criticism on Women” 71).

Martineau “believed in reform, not revolution,” which she knew was only possible if women and men alike were to face the narrow morals and expectations that society implemented. Kristeva points out that men and women’s “only difference is . . . [their] unwillingness to have a face-to-face confrontation with the abject,” which, arguably, is shame (209). The unwillingness to face the shaming of women caused the inability to offer women an education, for a fear of change in society. In her article “Woman,” Martineau points out the views that society associated with different subjects in relation to women. She states that, regarding philosophy, “she may pursue only fancifully, and under pain of ridicule;” regarding science as “only a pastime, and under a similar penalty;” considering art as “declared to be left open: but the necessary learning, and yet more, the indispensable experience of reality . . . denied;” and lastly regarding literature as “also said to be permitted, but under what penalties and restrictions?” While society held these beliefs in fear that an education for women would prohibit them from their sole duty of marriage, thus distributing the shame of education as being an unwanted identity, Martineau believed that women should be

educated so that they *could* be “better wives and housekeepers.” She believed that “it was a good political move to focus on issues that could unite women,” and “she wanted women to be true partners in their marriages,” according to Daniella Boucher in her article “Small victories, lasting change: Harriet Martineau, slavery, and women’s rights” (327). In other words, the shame of never reaching the high expectation of a housewife due to the distraction of education could, in fact, be used instead for women to better their home skills due to the intelligence they strive to achieve. Martineau did not necessarily wish to *change* the characteristics associated with womanhood, but she instead wished to encomb those characteristics in the embrace of a much yearned after education, which she believed society would be thankful for. In her autobiography, she states

Let them be educated, - let their powers be cultivated, to the extent for which the means are already provided, and all that is wanted or ought to be desired will follow of course. Whatever a woman proves herself able to do, society will be thankful to see her do, - just as if she were a man. (400-401).

In Martineau’s time, as in the 21st century, fear of accepting the possible benefits of change acted as a prominent force that stood in the way of both women and men even *considering* the need for a woman to be educated. Mary Wollstonecraft points out the passivity of the fear of education when she states in her *Vindication on the Rights of Women* that, when it comes to women’s

rights, the main principle is that “if she be not prepared by education to become the companion of man, she will stop of the progress of knowledge and virtue” (211). In other words, Wollstonecraft is stating that society forces women to “remain immured in their families groping in the dark” by denying them civil and political rights due to the belief that education will cause women to not fulfill their household duties, emphasizing the shame of their gender. Furthermore, Wollstonecraft claims that a woman’s gender causes her to be viewed as being in a “state of perpetual childhood” with a “weak elegance of mind, exquisite sensibility, and sweet docility of manners” (215). Wollstonecraft is pointing out that their lack of education causes women to be seen as children to their husbands instead of intellectual companions, or even friends. In other words, according to Wollstonecraft, “if women are not permitted to enjoy legitimate rights, they will render both men and themselves vicious,” in which the wife is seeking for a companionship with her husband as *more* than simply a housekeeper, yet her husband is incapable of seeing her as so (219). She states that the only way women can rise in the world (shamefully) is through marriage, which coincides with Martineau’s conception that the reliance on marriage causes the morals of women to be “fearfully ... crushed” from the “prevalent persuasion that there are virtues which are peculiarly masculine, and others which are peculiarly feminine” (“Women”). Both Martineau and Wollstonecraft are pointing out the societal views that certain qualities, specifically education, were specifically meant for men; women who wished to seek

those qualities were going against their societal womanhood. If the sole definition of society is based on the roles of its men and women, then to *change* those roles would raise an unsure societal future.

Contrary to belief, both men *and* women in Martineau and Wollstonecraft’s times believed that women were only meant to obtain the knowledge needed to excel in marriage. Women sought obedience over intelligence out of comfort, a concept that Wollstonecraft explains when she states in her *Vindication* that “blind obedience is ever sought for by power; tyrants and sensualists are in the right when they endeavor to keep women in the dark, because the former wants slaves and the latter a play thing.” According to Wollstonecraft, if society chose to “strengthen the female mind by enlarging it, there” would “be an end to blind obedience” as well as a woman’s dependence on a man as her protector (212). She further goes on to mock the entire idea that a man can completely act as a woman’s protector, considering that a woman’s shame from never reaching societal expectations will prove to her that a man cannot save a woman. Men’s promises “which they cannot fulfil” put women “off ... watch and defense,” causing a common wife sitting at home waiting for her husband to be, in actuality, less safe than she would be if she had duties outside household chores and the never ending wait for the return of her *educated* husband (“Woman”). If the masculine virtues of a man cannot fully save a woman from all of the perils of the world, then there is no viable reason why a woman should not take advantage of any education she can in order to better herself and the

future of her relationship. In the words of Mill, which Eileen Botting points out in her novel *Wollstonecraft, Mill and Women's Human Rights*, it was a "'moral crime' that women and children were not guaranteed a 'right' to 'education' ... because not only 'food' but also 'instruction and training for [the] mind' were necessary for individual well-being'" (116-117). Not only would the lack of education be depriving women the right to protect themselves, as according to Martineau, but according to Mill it would be depriving them of a substance equally important to the mind as food is to the body.

Martineau points out that because her society believes that "women have none of the objects in life for which an enlarged education is considered requisite, the education is not given" ("Woman"). She goes on to say in her essay, "Woman", that "intellect is dangerous" and "unfit," leaving marriage as the "only object left to woman." She does not cast down marriage in the eyes of women, however, Martineau boasts on it, stating that a wife of middle class or higher

has the best place in stage-coaches ... she hears oratorical flourishes on public occasions about wives and home, and apostrophes to woman: her husband's hair stands on end at the idea of her working, and he toils to indulge her with money ... in short, indulgence is given her as a substitute for justice ("Woman").

She is asserting that it is not the physical characteristics of marriage that shame women, but it is the effect of "conviction that the sum and substance of female education" which is based *solely* on an

intellect that does not exceed the duties of a housewife that creates shame. In fact, Wollstonecraft explains in detail exactly what this intellect, the only intellect expected to be possessed by women, consists of when she states that

Women are told from their infancy, and taught by the example of their mothers, that a little knowledge of human weakness, justly termed cunning, softness of temper, *outward* obedience, and a scrupulous attention to a puerile kind of propriety, will obtain for them the protection of man; and should they be beautiful, everything else is needless, for, at least, twenty years of their lives (217).

The only reason education is not deemed necessary for a woman *by* society is because of the simple duties a woman is confined to. In other words, the frivolous characteristics of marriage does not necessarily need to change. They need to be recognized as simply characteristics defining the marriage, not the wife.

Mary Wollstonecraft relates to Martineau's perception of the restrictions on a woman's marriage through emphasizing the unending cycle that a woman is put through as soon as she steps foot into society. Martineau states that, because of society's conception of what intellect women are permitted to obtain, "education gives this appearance of weakness," or shame, to females—a shame which women learn to accept in their youth. She points out that "in the education of women, the cultivation of the understanding is always subordinate to the acquirement of

some corporeal accomplishment” (220). While also having no “serious scientific study,” their eyes are soon turned to “life and manners” in which they “dwell on effects, and modifications, without tracing them back to causes.” In order to prove this, Wollstonecraft compares women to military men, “who are, like them, sent into the world before their minds have been stored with knowledge or fortified by principles” (220). Wollstonecraft states that soldiers are sent out into the battlefield with only the practice of “minor virtues with punctilious politeness” (220). The comparison bears the question: “Where is the sexual difference, when the education has been the same?” If women are sent out into the world with only the intellect of manners and opinions, then they are no different than the portion of their male counterparts who enter battlefields with no war experience, *except* through “the superior advantage of liberty, which enables the ... [latter] to see more of life” (221).

The advantage of liberty that soldiers, or men in general, possess not only allows them the weapon of a superior position in society to shame women, but it also overshadows them with a sense of pride that Martineau refers to as Crokerisms. In her “Criticism on Women,” Martineau describes the attacks from men who possess a “fear of the law of libel, and the rules of duelling,” specifically the duelling with women, and use this fear to mock the weaker specimens as Crokerisms, with the individual themselves being a Crokerite. Martineau states

Were a stranger to seek throughout the empire for the men who have

spared no woman who has dared to differ from them in politics—not even those across the purity of whose fame the breath of no slander but theirs was ever breathed—an Austen, an Edgeworth, or a Martineau,—for the men whom all manly men who speak the English tongue would clothe in recreant calf-skin, or substitute for the red stripes of the horsewhip,—he would find them in the Crokerites (68).

Martineau continues her representation of men who slandered women in her time for seeking to be educated as Crokerites by stating that women are “the most piquant and the safest objects of abuse a reviewer can select” due to not being protected “by law from the worst slander to which they can be subjected” (69). In other words, women *expected* to be shamed because of their place in society, making them easy and continuous targets for the Crokerisms of their male counterparts. The shame of the importance of beauty, manners, and the fact that “every affection of their natures rises up to make them use their influence to prevent their brothers and husbands from taking up their quarrel” allows Crokerites, subsequently society in general, to disrespect a woman’s entire morale.

Martineau believed that women could use the weaknesses that society, or Crokerites, viewed in them (their shame of being the lesser gender) to strengthen their determination to be better wives and mothers in addition to granting them with more power to seek education. Rachel Ablow points out in her article “Harriet

Martineau and the Impersonality of Pain” the importance of Martineau’s illnesses in both her writing and her life. She states that Martineau “used her illness as a source of rhetorical power” (678). In fact, Martineau wrote many essays addressing sickness, health, and “disability in explicitly personal terms,” which many critics consider “are bound up with philosophical questions about the nature of sensation, the specificity of pain, and perhaps most importantly, the relation between the individual and the social.” If the Crokerites, or society, were seen as the cause for illness while shame of gender was the illness itself, then according to Martineau’s conception of her own illness, a woman’s suffering from shame is the cause of a misunderstanding of her own experience. So, illness, or shame, is “the product of ignorance and thoughtless habit,” with ignorance representing the effect from a lack of education and thoughtless habit representing the unchanging societal process of homely duties a woman is confined to. Women do not need to *change* their place as wives and mothers in society, nor do they specifically need to change the opinions of the Crokerites. Instead, women need to understand that her experience as a woman in society is in no way related to her potential in other fields. Martineau’s deafness was an experience that she needed to realize should not affect her writing, and Queen Victoria’s beauty and youth should not have affected her rule. A woman’s place in society as the *weaker* and gentler gender should not affect her right to an education.

Martineau goes on to state that “the sufferer from illness,” or the woman suffering from shame, “is especially liable to error ...

because of the consistency with which the feelings of the ill tend to go unexamined” (681). In other words, the women suffering from shame—Martineau, Queen Victoria, and the common housewife— are especially liable to not seek a higher potential— writing, royal rule, and education— because the inequality attributed to them in society goes *unnoticed*. A woman’s lack of education is “by no means specific to her illness,” or shame, but is in actuality due to the “distorted perceptions” that “all sensations can produce” considering “all encounters with the world are open to error.” Ironically, society itself does not need to change, but instead the perception society has of *what* exactly it needs to be. Therefore, as Ablow states, “the goal of education is to minimize those distortions and errors as much as possible” (681). The potential of education goes beyond allowing women the opportunity to rise in society and unite in their marriages and motherhoods... The effect it would have on women has the potential to reveal the distorted perception of a society that believes the ailments, or shame, of a woman is enough to restrict her from rising above the shadow of her partner and seeking an education.

Martineau believed that education could allow women to reshape the “most basic aspects of ... perception and understanding,” prohibiting them from allowing their “ailments [that] often go unrecognized or improperly diagnosed” to shame them any further (Ablow 681). It is not necessary for societal perception to change in order for women to flourish as educated equals to men, but instead quite the contrary. It is necessary for societal perception to be

embraced as a *distorted* perception, in which the shame that is associated with what is *believed* to be the intended nature for a woman is actually a flame that can spark her determination to “exercise freedom of mind in deciding upon what duty is, and the methods by which it is to be pursued” (Martineau 293). To Martineau and Wollstonecraft alike, education is the key to changing the distorted perception of both society and the individual perception that a woman has of the gender based characteristics that shame her. Merleau-Ponty paints this picture of shame through his metaphor that, in societal “perceptual communication,” a woman is a portrait consisting of “a familiar face with an expression which is immediately understood.” He continues to say that the face only expresses its meaning through “the arrangements of the colours and lights which make it up, the meaning of the gaze being not behind the eyes, but in them....” According to Merleau-Ponty, a “touch of colour more or less is all the painter needs in order to transform the facial expression of a portrait...” And a touch of education is all that women need to transform their distorted perception that *society* views when gazing at the portrait of women as a whole.

References

- Ablow, Rachel. “Harriet Martineau and the Impersonality of Pain.” *Victorian Studies*, vol. 56, no. 4, 2014, pp. 675–697.
- Susan F. Bohrer. “Harriet Martineau: Gender, Disability and Liability, Nineteenth-Century Contexts,” 25:1, 21-37, DOI: 10.1080/0890549032000069122
- Botting, Eileen Hunt. *Wollstonecraft, Mill, & Women’s Human Rights*. Yale UP, 2016.
- Boucher, Daniella. “Small victories, lasting change: Harriet Martineau, slavery, and women’s rights.” *Human Architecture: Journal of the Sociology of Self-Knowledge*, vol. 4, 2006, p. 321+. *Academic OneFile*, http://link.galegroup.com/apps/doc/A227997819/AONE?u=tel_a_ttul&sid=AONE&xid=db42bd07. Accessed 24 June 2018.
- Brown, Brené “Shame Resilience Theory: A Grounded Theory Study on Women and Shame.” *Families in Society*, vol. 87, no. 1, 2006, pp. 43–52.
- Butler, Judith. *Gender Trouble : Feminism and the Subversion of Identity*. Routledge, 1999.
- Fox, Nick J. *The Body*. Polity Press, 2012.
- Kristeva, Julia. “Powers of Horror,” trans. by Leon S. Roudiez (New York: Columbia UP, 1982) (1982): 1-31.
- Martineau, Harriet. *Autobiography*, with Memorials by Maria Weston Chapman, 3 vols, London: Smith, Elder 1877.
- . “Criticism on Women.” Edited by Gayle Graham Yates, Rutgers UP, 1985.
- . *Society in America*. Edited by Seymour Lipset, Doubleday, 1968.
- . “Woman.” 1837. *Quotidiana*. Ed. Patrick Madden. 12 Feb 2007. 08 Jul 2018 <<http://essays.quotidiana.org/martineau/woman/>>.

Merleau-Ponty, Maurice. *Phenomenology of Perception*. Translated by Colin Smith, Routledge Classics 2002.

Nussbaum, Martha. "The Professor of Parody," *The New Republic Online*, thenewrepubliconline.com, Accessed 24 July 2018.

Wollstonecraft, Mary. "A Vindication of the Rights of Woman." *The Norton Anthology of English Literature*, edited by Stephen Greenblatt, Version 9, vol. 2, W.W. Norton & Company, 2012, pp. 211-239.

An Evaluation Protocol for Transforming Shelter Dogs to Service Dogs

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Abstract

The goal of this project was to see if shelter dogs within the Cookeville/Putnam County Animal Shelter could be reliable candidates for service work. We did this by evaluating over fifty dogs in hopes of not only finding a suitable candidate, but also pursuing training in Peanut Detection work with the dog selected. The evaluation process took persistence, patience, and an open mind considering that many of the dogs in the shelter have little to no human interaction and are severely lacking manners and a foundation in basic obedience. We found that the dogs who showed the most promise were five months old or younger. We also found that the dogs needed to possess some form of food or toy drive to initiate engagement with the handler. If the dogs found no value in the reinforcer, they would lose interest and self-reward on their environment. Factors that also played a significant role in the elimination process were behavioral issues such as fear, dog aggression, food aggression, possessiveness of his/her belongings, lack of confidence in new locations, over stimulation, and, of course, no motivation for the reinforcement we presented. Through this process we did find a few promising dogs and narrowed it down to one. Parker, a four-month-old hound mix who was introduced to peanut odor at five months of age. He showed great progress and is still pursuing training in peanut detection work. He is now nine months of age and is enjoying training and bonding with his potential adopter who suffers from severe peanut allergies.

Keywords: peanut allergen, peanut detection dog, shelter dog

Introduction

The driving question of this research was to determine if shelter dogs could be reliable candidates for service work. Shelters can be a very stressful environment for animals. Constant barking and little human interaction are just some of the factors that can affect the behavior of these dogs (Hines, 2003). These factors can affect behavioral stability, an important attribute in a service dog because the handler needs a reliable dog that can be trusted in any situation. There are 3.3 million dogs in animal shelters

across the country at a given time (ASPCA, 2018); there are also many individuals who need service dogs but cannot afford them. Training shelter dogs could be a great help to these people in terms of finances and availability. Not only could trained shelter dogs be a great benefit to an individual in need, but it could also help the community as a whole by training shelter dogs to be good citizens.

We predicted that suitable shelter dogs can be found that can be transformed into service dogs, specifically in the field of

peanut detection. We chose peanut detection work for this project because of the great need and demand of these dogs within individuals suffering from peanut allergies. A second reason is the very high expense of these dogs – a good peanut detection dog (PDD) can cost anywhere from \$10,000 and up, depending on the advancement and the time put into the dog (Gibeault, 2017).

Objectives

The end goals of this research were to:

1. Determine if shelter animals are reliable candidates for service work.
2. Temperament test and evaluate every dog in the shelter, in turn helping them be placed in a perfect home.
3. Once the dog is selected, begin extensive training in peanut detection and public access.
4. Have a reliable “started” dog in the training process of becoming a PDD.
5. Place the dog in a home with a participant suffering from peanut allergies.

Methods

Selection of Scent Work Candidates

The first month of the research project consisted of evaluating dogs at the Cookeville/Putnam County Animal Shelter (CPCAS). This was a large task, as during the first week there were 52 dogs that required initial evaluation. One factor that

played a role in the selection process was that the dogs had to have ball drive. Simply stated, they had to have the desire to chase a ball since the ball was the main reinforcer in peanut detection training. The reasoning for this is two-fold. First, many dog foods and treats are manufactured in factories that have peanut products. This process could, in turn, leave a residual odor of the peanut in the treats given to the dog. Second, the dogs will have to work and stay focused in the presence of different types of food (without eating it). To create clear communication and to narrow the risk of confusion in the learning process, the only reward used was the ball. This step came as a challenge considering that many of the dogs did struggle with engagement, which became more difficult with a toy they had never seen before. The dog’s drive level was measured on the first evaluation form so engagement with the trainer could be immediately evaluated. Both toy drive and food drive were measured on a scale ranging from one to ten, one being no drive, and ten being substantial drive for the reinforcer.

Many of the dogs did not move into the next step of evaluation due to behavior issues such as food or dog aggression. These behavior issues could not be overlooked and must be addressed for a potential service dog (Poulsen, Lisie, & Phillips, 2010). To test food aggression, we used a Humaniac™ Helping Hand (see Figure 1), which is a plastic hand extension to safely place into a dog’s bowl as they eat. An initial evaluation of dog aggression involved observing the dog’s behavior when walking by the kennel area (Slater, Weiss, & Mohan-Gibbons, 2012).



Figure 1. Testing food aggression

During phase two, dog aggression was further tested. To accomplish this, two dogs were fitted with basket muzzles and put on a 20-foot line to greet each other in a safe manner. The dogs were also taken to a new location outside of the shelter to further evaluate them during this phase of the project. By the third phase, the candidate pool had been narrowed to three dogs, each under the age of five months. All three of these dogs were introduced to the odor source and were also taken to new public locations. During phase four, a single candidate was selected (Figure 2) and

fostered to prepare him for a home environment. He was also taken to new locations frequently to generalize his skill sets with a higher distraction threshold. A potential adopter with peanut allergies was also contacted during this stage.

Overcoming Environmental Factors of Scent Detection

Odors were frequently changed to prevent contaminations such as trainer's personal odor, the dog's saliva, or other foods. One must be aware of contaminants and the residual odors present in detection training. Because of dogs' very powerful olfactory receptors, they can smell everything in layers, i.e., they can smell even the container the scent is held in, as well as their own scent and the handler's scent (Correa, 2016). Unknowingly, the dogs could eventually be imprinted on certain containers, or even their own saliva. To counteract this potential confusion, the containers were cleaned after every use in a bleach bath. Then to ensure the dog did not become imprinted on bleach or the odor of the container, blank hides were set up. In this process, the container was bleached and touched with the trainer's odor, then treats used in training were added. Lastly, a sample of the dog's saliva was applied to the blank hide. Often the dog indicates on this blank, but this does not lead to reinforcement; therefore, the dog learns the irrelevance of these odors.

Training Process for Final Candidates

When candidates had been selected to begin training in peanut detection, they were imprinted to odor in a low distraction environment in the shelter (see Figure 3).

Evaluation Process for Peanut Detection Training

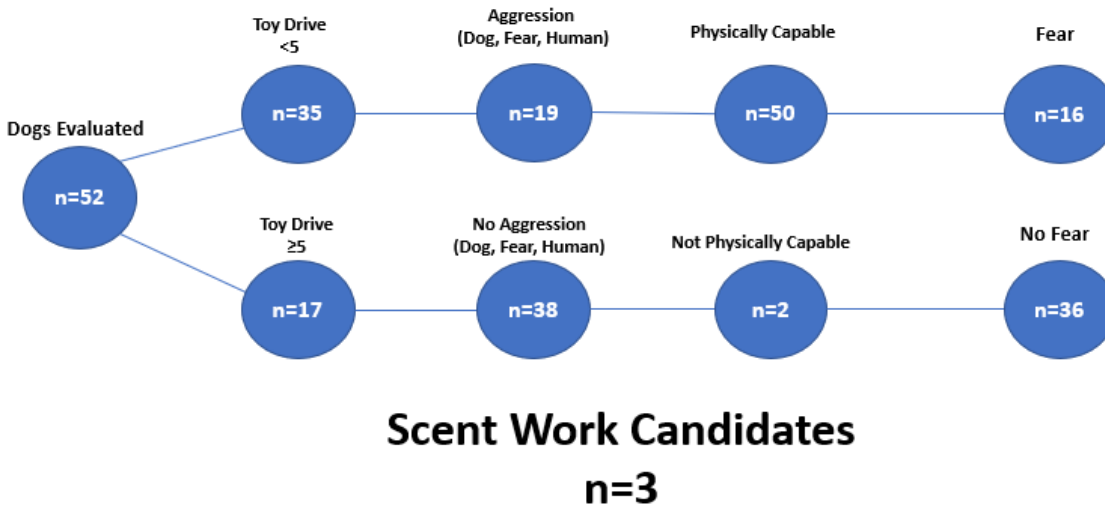


Figure 2. Evaluation decision tree.



Figure 3: Parker working at the CPCAS

Classical conditioning was utilized in this research project when imprinting the dog to odor source. Classical conditioning is simply creating a positive or negative correlation between a neutral stimulus that holds no value and pairing it with a potent stimulus that holds a lot of value to the dog (Jenkins, Barrera, Ireland, & Woodside, 1978). For this study, a value in peanut odor was desired. Classical conditioning was utilized by pairing the neutral stimuli (the odor source) with the potent stimuli (the reinforcer) repeatedly until the dog created a positive correlation to the neutral stimuli making it a secondary reinforcer. At this point in the training, the odor held such a positive meaning to the dogs that it, in itself, was reinforcing the response to search an area effectively. After the dogs became

constant with targeting the odor, the visual help was taken away to make the hides more challenging. During step two, the dogs learned to use their noses rather than their eyes. This process was conducted in a very low distraction environment to ensure the dogs could be successful. When the dogs were consistently targeting odor in a low distraction search area, training was expanded to new locations, making the dog and its work functional in everyday situations. In step three, the candidate pool was narrowed from three dogs to one dog to focus more on generalization and proofing of the learned response. To successfully do this, the selected dog was moved from the shelter environment into a home setting. The researcher began to foster the selected dog two months into the project. This move was a significant transition for the selected dog considering he had never known anything but a kennel run. Therefore, the main training focus was potty training and learning to be a normal dog in a home. While living with the researcher, he was able to be exposed to new locations and work in totally new areas. During this time, the selected dog was practicing his skill sets

(detection and obedience) in low distraction public locations (see Figures 4 and 5).

This situation was not an issue for the selected dog due to his high food drive and engagement with the handler. He did struggle when the distraction threshold was raised during his training sessions. When struggle was noted with new distractions, training was simplified to allow for increased success. When he was around eight to nine months old, a small apprehension in large crowds was noted, however, this is a normal response, especially in this age range. During this time in the training process, it was clear and the obedience training pace needed to be slowed in order to focus on building confidence. When too much pressure and expectations are placed on a young dog, the stress can in turn create lack of confidence. To combat this, he was taken to fun places and allowed to express himself and relax. The selected dog did grow out of this, and after that initial time period, a focus was placed on more control in his obedience routine. The training protocol for the final candidate for service work is shown in Figure 6.



Figure 4. Parker working in new locations



Figure 5. Parker working on public access

Training Method Used

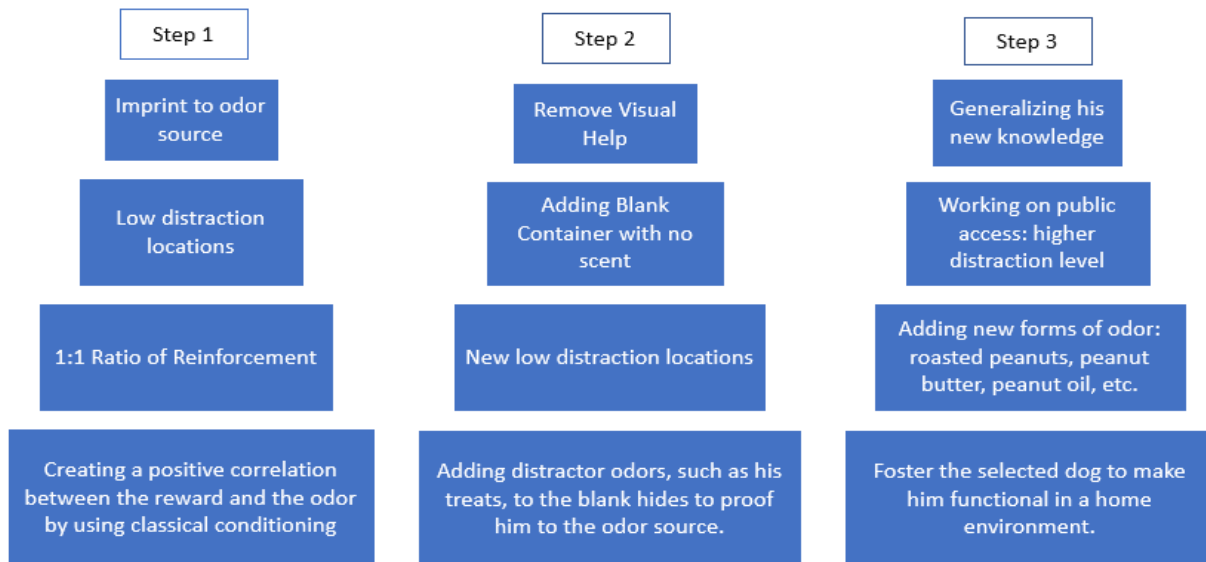


Figure 6. Training protocol for selected service dog candidate

Results

Out of the 52 dogs evaluated during the first phase, 35 dogs were found to have ball drive less than five, while only 17 dogs had toy drive greater than or equal to five. Only ten dogs out of the 52 dogs had enough ball drive for it to be a valuable reinforcer for good behavior. Out of the 52 dogs evaluated, there were six dogs who went to the second step of evaluation. After the second round of evaluation, only three dogs advanced to the next round. The other three dogs did not pass for a variety of reasons, including lack of endurance, lack of engagement in new locations, and the inability to concentrate in the presence of other dogs. There were four rounds of evaluation all together that the remaining dogs had to pass to be considered a reliable candidate for service work.

The results of the three selected dogs were astounding and exceeded expectations. The dogs selected had an exceptional hunt drive that was able to be developed at an accelerated rate during the summer project. After a few weeks of further training and exposure, Parker, a hound mix, was selected to pursue peanut detection training. He was four months old when training for service work was initiated. He exhibited high food and toy drive which meant he was ready to work and engage in any situation. The main issue in the training process was not in the detection training, but rather his ability to remain calm around other dogs, as he was always ready to play with them. Due to his high drive, which is needed in this training, he struggled to find his off switch in everyday situations. Of course, his very young age likely had an influence on his behavior. Some of these issues can be

resolved through maturity and slowly incorporating these high distractions into his training routine. However, the most progress in this pursuit was noted when the researcher took Parker home as a foster to continue his training (see Figure 7). Parker was successfully indicating raw peanuts, roasted peanuts, peanut butter powder, and peanut oil by the end of this project, with little to no visual help.

Final Candidate Summary of Characteristics and Further Training

Characteristics of our final candidate, Parker, were:

1. Young: started at four months old
2. High food and toy drive
3. Friendly, playful, and engaging
4. Easily distracted

Parker's training and eventual placement will be enhanced with the following:

1. Training with distractions
2. Maturation time
3. Reinforcing toy/ball drive

Conclusion

It was found that many of the dogs at the shelter are not suitable candidates for service work; however, through many evaluations, time, and patience, it is possible to find a suitable candidate. Many of the dogs had wonderful qualities, whether that be in service work or simply as a loving pet. The majority of dogs evaluated had some fear and confidence issues, possibly due to the

shelter environment in which they are living. Through the duration of the research project, some dogs with behavioral issues were trained in basic obedience to see how they progressed. Through training, most of these dogs showed significantly improved behavior, which increased their chances of adoption.

Young dogs were found to be more inclined to engage in training. Research did not indicate that any specific breed was more suitable than another for service work; however, Parker (a hound mix) was very responsive to detection work and had a great hunt drive. Following the summer training session, Parker continued to advance in his scent detection training and has been working with adults suffering from severe peanut allergies (see Figure 8.)



Figure 7. Parker at his foster/researcher's home



Figure 8. Parker and practicing handler

Acknowledgments

I would like to thank the Cookeville/Putnam County Animal Shelter for allowing me to work with all their dogs. I appreciate The Save Us Club and its members for supporting this hands-on experience. The authors are thankful for the financial support from the Creative Inquiry Summer Experience (CISE) fund. This fund was a part of the Quality Enhancement Plan (QEP) at Tennessee Technological University.

References

ASPCA. (2018). Pet statistics. Retrieved from <https://www.asPCA.org/animal-homelessness/shelter-intake-and-surrender/pet-statistics>

Correa, E.J. (2016). The dog's sense of smell. Retrieved from <http://www.aces.edu/pubs/docs/U/UNP-0066/UNP-0066.pdf>

Gibeault, S. (2017). Peanut detection dogs save lives. Retrieved from <https://www.akc.org/expert-advice/lifestyle/peanut-detection-dogs-save-lives/>

Hines, L. (2003). Historical Perspectives on the Human-Animal Bond. *American Behavioral Scientist*, 47(1), 7-15.

Jenkins, H.M., Barrera, F.J., Ireland, F., & Woodside, B. (1978). Signal-centered action patterns of dogs in appetitive classical conditioning. *Learning and Motivation*, 9(3), 272-296.

Poulsen, A., Lisle, A., & Phillips, C. (2010). An evaluation of a behaviour assessment to determine the suitability of shelter dogs for rehoming. *Veterinary Medicine International*, 2010, 523781.

Slater, M., Weiss, E., & Mohan-Gibbons, H. (2012). Preliminary investigation of food guarding behavior in shelter dogs in the United States. *Animals*, 2(3), 331-346.

Weiss, E. (2002). Selecting shelter dogs for service dog training. *Journal of Applied Animal Welfare Science*, 5(1), 43-62.

Synthesis and NMR Characterization of Pyruvaldehyde bis-tertbutylthiosemicarbazone

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Abstract

Pyruvaldehyde was reacted with a 4-tertbutyl-3-thiosemicarbazide to give a unique bis-thiosemicarbazone compound named pyruvaldehyde bis-tertbutylthiosemicarbazone, with the acronym PYR-tBTSC. This compound was characterized by NMR studies, $^1\text{H-NMR}$, $^{13}\text{C-NMR}$, $^{15}\text{N-NMR}$, $^{15}\text{NHSQC}$, and $^{13}\text{CHSQC}$ on a 500 MHz NMR spectrometer. Due to the asymmetrical nature of pyruvaldehyde, the structure of the compound can be easily derived.

Introduction

Thiosemicarbazones and their derivatives are compounds that have developed great interest for their anti-microbial and anti-cancer properties, biological activities, and metal-chelating properties. (1-3) These ligands can be reacted with metal ions, primarily Cu^{2+} in this series, and also used as anti-microbial agents. (4) The metal complexes are formed with a square planar geometry around the metal atom due to the connectivity of the transition metals. This property allows for a consistent geometry with many different metal ions. One of

these complexes, copper pyruvaldehyde bis-methylthiosemicarbazone (CuPTSM), has been used as an imaging agent for PET scans since the late 1980's. (5) It has been shown in the literature to have an increased uptake in brain and tumor tissues. (6) This compound has been thoroughly studied and it is believed that copper complexes of other bis-thiosemicarbazone ligand derivatives may have similar activity. The synthesis and NMR data on one of these ligands has not been properly studied or classified with the various NMR experiments.

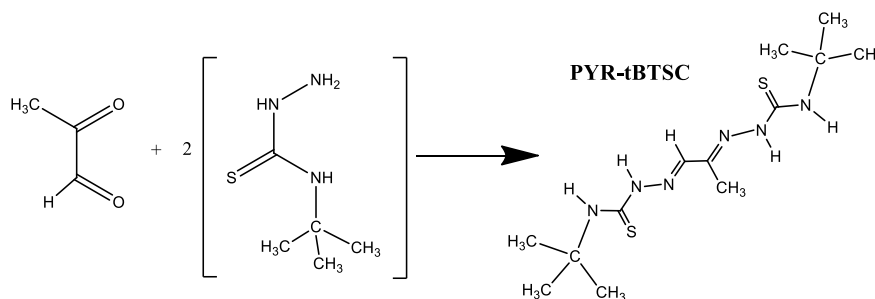


Figure 1. Synthesis of PYR-tBTSC

This work presents the synthesis of a new bis-thiosemicarbazone compound not found in the literature, pyruvaldehyde bis-tertbutylthiosemicarbazone (PYR-tBTSC). Figure 1 provides a structure for this compound. Evidence for the structure of this compound was acquired by using ^1H NMR, ^{13}C NMR, and the 2D experiment ^1H - ^{15}N HSQC (heteronuclear single quantum coherence) NMR spectroscopy. This data was then compared to the ethyl and methyl derivatives of this compound for further verification and validation (Figure 2).

Experimental Section

The pyruvaldehyde, as well as the 4-tertbutyl-3-thiosemicarbazide, were both purchased from Sigma-Aldrich Chemical Company. All other reagents and solvents used for the synthesis were purchased from Sigma-Aldrich. All materials used were either reagent grade or better and were not purified any further. The NMR spectra were obtained on a Bruker Ascend-500 Multi-Nuclear NMR spectrometer.

Synthesis of PYR-tBTSC, [pyruvaldehyde(bis)tertbutylthiosemicarbazide]

2,2'-(1-tertbutyl-1,2-ethanediylidene)bis[*N*-methyl-hydrazinecarbothioamide]

In a 125mL Erlenmeyer flask, equipped with a magnetic stir bar, was added 0.424g (2.88×10^{-3} mol) of 4-tertbutyl-3-thiosemicarbazide, and 30mL of a 5% acetic acid solution to create a slurry by stirring on a hot plate. Next, 0.255g (1.41×10^{-3} mol) of a 40 wt% solution of pyruvaldehyde (PYR) was added to the reaction mixture. The hot plate was heated to 60 °C and the reaction mixture was left overnight with constant stirring. The pale-yellow product that precipitated was then filtered and dried.

The yield was 0.401g (1.21×10^{-3} mol) 86.15% PYR-tBTSC.

^1H NMR (300 MHz, d6-DMSO); 11.52, 10.35, 7.72, 7.69, 7.52, 3.34, 2.11, 1.50.

^{13}C NMR (126 MHz, DMSO) 175.86, 175.31, 145.88, 141.39, 52.88, 28.41, 11.18.

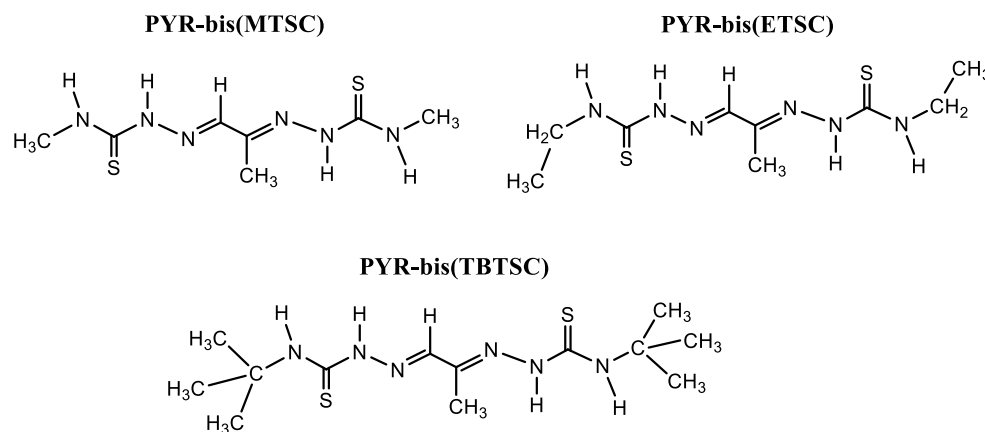


Figure 2. Structural Comparison of PYR-TSC derivatives discussed in this paper

Results and Discussion

Pyruvaldehyde bis-tertbutylthiosemicarbazone has not been previously reported in the literature. The synthesis procedure that was used for production of this ligand, see Figure 1, proceeds to give high yield and high purity of the product. The methyl and ethyl derivatives of this compound, see Figure 2, has been reported and extensively studied. (4-7)

PYR-tBTSC is just one ligand in a family of ligands, some of which have been extensively studied as previously mentioned. As these ligands are closely related, the data acquired in this study can be compared to that in the literature to further verify the structure and conclusions.

The ^1H NMR spectrum for PYR-tBTSC is very clean and gives a clear picture of the resonance frequencies of the protons that can be correlated to the proposed structure. Figure 3 provides correlation information of the ^1H NMR spectrum to the proposed structure.

Due to the electron donating or withdrawing characteristics of different substitutes on the ligand, different resonance shifts of the protons will be noted. This is due to shielding characteristics that result in either a more upfield or downfield shift. This property becomes vital in distinguishing different substitutes and will allow for a better comparison with the ligands in the literature (Table 1).

The asymmetrical nature of pyruvaldehyde makes labeling each of the hydrogen locations a much simpler task, as the compound can be split into two distinct arms. One arm has a methyl group on the backbone of pyruvaldehyde and will thus have a more upfield set of protons compared to the arm that has the imine hydrogen on the backbone. Typically, a methyl group is considered to be more electron-donating compared to a hydrogen atom, thus it shields the protons on and near it more than a hydrogen atom, thus their resonance frequencies are more upfield (i.e. nearer to zero ppm). This distinction is most dramatic with the protons closest to the imine

Table 1. Comparison of Selected ^1H NMR Resonance Peaks

COMPOUND	HYD-1(A)	HYD-2(B)	THIO-1(C)	THIO-2(E)	IMINE
PYR-tBTSC	11.52	10.35	7.72	7.49	7.52
PYR-MTSC	11.71	10.31	8.49	8.38	7.65
PYR-ETSC	11.59	10.17	8.44	8.34	7.65

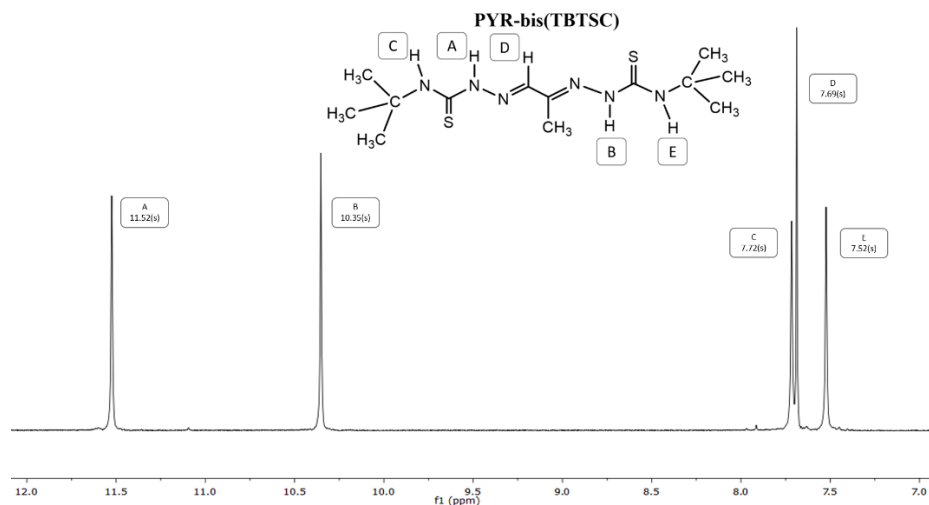


Figure 3. Downfield ^1H NMR Spectrum of PYR-tBTSC

hydrogen. The proton labeled A (Figure 3) resonates much further downfield, at 11.52 ppm, than the corresponding proton labeled B, 10.35 ppm. These peak locations are nearly identical to the other ligands in the series as well, (Table 1). The thioamide protons show a bit of a different result than the other ligands, and it is believed this is because of the bulky nature of the tertbutyl group. The thioamide protons become more shielded and resonate about 1 ppm upfield. The separation between the thioamide protons is still seen with C at 7.72 ppm and at 7.49 ppm. The imine hydrogen itself resonates at 7.52 ppm, and this is, once again, similar to the other data for PYR-MTSC and PYR-ETSC as seen in Table 1. The upfield portion of the ^1H NMR for this compound is not shown (Figure 3) as it is less relevant for the overall structure identification, but this information is provided in the Experimental section. The methyl group resonates at 2.1 ppm. The protons in the tertbutyl group are the furthest away from the asymmetry caused by the

imine proton and the methyl group on the pyruvaldehyde backbone and are, therefore, the least affected and show little change in resonance frequency as expected. The two sets of tertbutyl protons, therefore, resonate as a pair of singlets at about 1.50 ppm, and each of the peaks integrates to the nine hydrogens expected from a tertbutyl group.

Conclusions

The pyruvaldehyde bis-tertbutylthiosemicarbazone ligand has been readily synthesized with high yield and purity of the product. The ^1H -NMR of the ligand shows the correlations of various proton resonances that coincide with the proposed structure. Our results are also verified by the data obtained in the literature for the analogs PYR-MTSC and PYR-ETSC.

Now that the ligand has been synthesized and characterized further research can be done by using this ligand to synthesize transition metal complexes. Work has

already begun in synthesizing copper, nickel, and palladium complexes of this ligand. Multiple NMR experiments are planned for each of the applicable metal complexes as well as their biological activity. This data and further work will be reported in a future journal article.

Acknowledgements

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References

1. Beraldo, H.; West, D. Copper(II) and nickel(II) complexes of pyruvaldehyde bis{N(3)-substituted thiosemicarbazones}. *Transition Metal Chemistry* 1997, 22, 294-298.
2. Green, M. A.; Klippenstein, D. L.; Tennison, J. R. Copper(II) Bis(thiosemicarbazone) Complexes as Potential Tracers for Evaluation of Cerebral and Myocardial Blood Flow with PET. *The Journal of Nuclear Medicine* 1988, 29, 1549.
3. R. M. Michaels; L. J. Peterson; G. L. Stahl The Activity of Substituted Thiosemicarbazones against *Trichomonas vaginalis* and *Trichomonas foetus* In vitro and in Experimental Animals. *The Journal of Parasitology* 1962, 48, 891-897.
4. Jason S Lewis; Judith M Connett; Joel R Garbow; Thomas L Buettner; Yasuhisa Fujibayashi; James W Fleshman; Michael J Welch Copper-64-pyruvaldehyde-bis(N(4)-methylthiosemicarbazone) for the prevention of tumor growth at wound sites following laparoscopic surgery: monitoring therapy response with microPET and magnetic resonance imaging. *Cancer research* 2002, 62, 445-449.
5. Liu, J.; Hajibeigi, A.; Ren, G.; Lin, M.; Siyambalapitiyage, W.; Liu, Z.; Simpson, E.; Parkey, R. W.; Sun, X.; Oz, O. K. Retention of the Radiotracers ^{64}Cu -ATSM and ^{64}Cu -PTSM in Human and Murine Tumors Is Influenced by MDR1 Protein Expression. *The Journal of Nuclear Medicine* 2009, 50, 1332-1339.
6. Beraldo, H.; West, D. Copper(II) and nickel(II) complexes of pyruvaldehyde bis{N(3)-substituted thiosemicarbazones}. *Transition Metal Chemistry* 1997, 22, 294-298.
7. Lewis, J. S.; Connett, J. M.; Garbow, J. R.; Buettner, T. L.; Fujibayashi, Y.; Fleshman, J. W.; Welch, M. J. Copper-64-pyruvaldehyde-bis(N4-methylthiosemicarbazone) for the Prevention of Tumor Growth at Wound Sites following Laparoscopic Surgery: Monitoring Therapy Response with microPET and Magnetic Resonance Imaging. *Cancer Research* 2002, 62, 445.
8. National Science Foundation (NSF) Major Research Instrument (MRI) 1531870: Acquisition of a 500 MHz NMR Spectrometer (2016, Dr. Jesse Carrick P.I.).

Optimization and Kinetics of Gradient Polyacrylamide Gel Formation

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Abstract

Polyacrylamide gel electrophoresis (PAGE) is a biochemical separations technique most commonly employed for the separation of water-soluble proteins that are to be analyzed with further methods. A more useful form of this technology is when it employs the use of a concentration gradient of the polymer material throughout the length of the gel that is cast, which makes its separation capacity increase significantly. Formation of these types of PAGE gels is a painstaking process when done by hand—a trend that leads most laboratories to purchase pre-cast gels formed industrially due to the control that can be achieved in those processes. Our goal has been to understand the kinetics of these gradient formations as they occur in hand-based polymerization methods, as well as to explore the kinetics of the cross-linking reaction in a batch-based manner, so that an accurate model for simulations can be done on changes to the polymerization process. Further, we have examined how laboratories on a budget can achieve successful formations of gradients using additively manufactured materials and re-purposed labware.

Introduction

Polyacrylamide Gel Electrophoresis (PAGE)

The process reviewed in this communication pertains to the separation of proteins—the fundamental machinery of life—using a technique known as Polyacrylamide Gel Electrophoresis (PAGE). Moreover, we examine the formation of cross-linked polyacrylamide—the main polymer material used to perform separations of water-soluble proteins in an electrophoresis chamber. PAGE is used both in native and in surfactant-containing media (e.g. gel matrix, buffer solutions). Native PAGE (NAT-PAGE) is the use of PAGE without the addition of sodium dodecyl sulfate (SDS)—

a surfactant and/or detergent that is used to make the charges on the periphery of a protein uniformly negative. PAGE processes that use SDS are referred to as SDS-PAGE.

A third important type of PAGE to consider is its use in 2-D PAGE separations. In a 2-D PAGE separation, an isoelectric focusing gel is inoculated with a protein sample and run according to the parameters for the specific IPG strip used in the process. The strip is then adhered to a NAT- or SDS-PAGE using a hydrocolloid solution of agarose[1]. Agarose is a carbohydrate that is used in DNA and RNA separations[2]. It differs from PAGE gels because it has no physical crosslinks. Instead, the matrix is held

	NAT-PAGE	SDS-PAGE	2-D PAGE
USES	<ul style="list-style-type: none"> • Studying protein complexes • Quick separations for immediate visualization of simple mixtures 	<ul style="list-style-type: none"> • Separating proteins by molecular weight • Preparative separations for downstream LC-MS 	<ul style="list-style-type: none"> • Separating protein complexes • Special assays • Complex mixtures requiring molecular weight separations
ADVANTAGES	<ul style="list-style-type: none"> • Separates proteins based on charge and molecular weight 	<ul style="list-style-type: none"> • Reduces separation to one only related to molecular weight 	<ul style="list-style-type: none"> • 2D separation that includes pH component and molecular weight components • Tool that is useful for drug complex assays (native 2D)
DISADVANTAGES	<ul style="list-style-type: none"> • Resolution may suffer due to mass-to-charge ratio interferences 	<ul style="list-style-type: none"> • Proteins cannot be used in charge-specific applications once processed this way 	<ul style="list-style-type: none"> • Resolution can suffer due to issues with sample loading • Resolution can suffer due to mass-to-charge interferences

Table 1. Uses, Advantages and Disadvantages of PAGE Gels

together by hydrogen bonding, which is a strong intramolecular force, but is still more easily broken the physical crosslinks of polyacrylamide gels[3]. The pore size of agarose is much larger than that of polyacrylamide, so using it as the glue for a 2-D PAGE gel allows adequate transfer between the two differing gels in the process.

The major uses, advantages and disadvantages of the different PAGE methods are summarized in Table 1 in order to provide context for them. This review is not exhaustive and is simplified to the three main types of gels used in these separations.

In the past 20 years, there have been many other sub-specialized PAGE applications. A current trend is the exploration of nanoparticle-enhanced gels that may have increased resolution, durability, and shelf-life[4,5,6]. Microfluidic technologies using PAGE as a media are currently being used in separations of various biomolecules. Notwithstanding, most major proteomics laboratories are trending toward the use of LC-MS for their data and PAGE is now being used mostly to aid that process[7,8].

Polyacrylamide vs PAGE gels

Polyacrylamide is actually an ambiguous term for the polymer it can refer to in a

general context. The IUPAC rules for polymer naming allow for two specific names in the case of a PAGE gel because the PAGE gel is a co-polymer containing acrylamide and bisacrylamide (both common names for the compounds in the synthesis) in an unidentified or unknown pattern. The formal IUPAC name in this case would be poly(2-prop-enamide-*co*-N-[(prop-2-enoylamino)methyl]prop-2-enamide); however, the IUPAC rules for polymer naming also allow the use of common and/or traditional names for monomers in the polymer, so a simpler and suggested name would be poly(acrylamide-*co*-bisacrylamide)[9]. In this communication, the abbreviation PACB will be used to refer to the latter of the two IUPAC names.

It is important to apply IUPAC naming conventions because in the absence of appropriate context the name (polyacrylamide) can mean different things depending on the reader. Based on IUPAC rules, “polyacrylamide” means a *macromolecule* of acrylamide that is not size specific, nor construction defined[10]. The IUPAC rules say that a polymer name must have the prefix *poly* before an enclosure that contains the monomers of composition. Therefore, a polymer of acrylamide monomers would be named poly(2-prop-enamide) or poly(acrylamide). As a case in point, several papers in the literature reviewed for these projects detailed experiments in which the kinetics of a free radical polymerization were determined for poly(acrylamide) using different catalysts. These papers dealt with only a polymer

composed of acrylamide monomers and not the crosslinked counterpart encountered in journals of the American Chemical Society and in major proteomics, biomolecular, and even polymer journals. The use of IUPAC nomenclature is not habitual in many publications, and so this can present challenges when evaluating the viability of various methods and/or applications of the findings of researchers to new problems unless their context is heavily considered.

In either case, poly(acrylamide) and poly(acrylamide-*co*-bisacrylamide) are both hydrogel polymers because they are water soluble and tend to undergo gelling in solution as more polymer chains or crosslinks form. The method of polymerization is typically a free radical polymerization method that involves a persulfate radical generator such as ammonium persulfate (APS) or potassium persulfate (KPS) in the presence of N,N,N,N-tetramethylethylenediamine (TEMED)[11]. A photochemical polymerization method is also an option to initiate the radicals for the method. The most reported initiator being riboflavin-5'-phosphate (riboflavin)[12]. These initiators are all chosen due to their solubility in water—a necessary feature if polymerization is to occur since only particles in solution can react. These reaction schemes are summarized in Figure 1.

Characterization of PAGE Gels

Hydrogels are characterized by the Percent T (% T; Eqn. 1) and Percent C (% C; Eqn. 2). This method is important even in commercial literature on PCAB, and in the

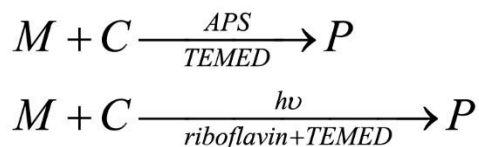


Figure 1. Reaction Schemes for PAGE Gels. (top) Scheme for a typical solution-based generation of radicals that utilizes the persulfate ion system to generate free radicals and induce polymerizations. The method is the most common but is actually more sensitive to oxygen in solution than other methods. (bottom) Scheme for the photochemical induction of radicals using the riboflavin system. The excitation wavelength for this reaction may fall somewhere between 365 nm to 400 nm because the excitation range for riboflavin is fairly responsive throughout that band of wavelengths. The use of the photochemical method avoids problems with dissolved oxygen but takes somewhat longer—the initiator does not have to be as concentrated in this method.

market of products for biomolecular researchers further terms have been developed to define these relationships—often times without appropriate literature explanations of their meaning. An attempt has been made in this communication to clarify such measures of concentration.

$$\%T = \frac{m_M + m_{CL}}{V_{H_2O}} \times 100 \quad (\text{Eqn. 1})$$

$$\%C = \frac{m_{CL}}{m_M + m_{CL}} \times 100 \quad (\text{Eqn. 2})$$

In Eqn. 1 and Eqn. 2, m_m is the mass of monomer, m_{cl} is the mass of crosslinker, and V_{H_2O} is the volume of water in which the monomer and crosslinker are dissolved. These two equations are the most commonly used characterizations for hydrogels of any type that contain physical crosslinks[13]. Another method is often used in PACB gels industrially, and the number derived is even

used as a way to purchase specific precast gel materials or handcasting solutions from major suppliers. The measure in question (Eqn. 3) is best referred to as the monomer-to-crosslinker ratio (MCR).

$$MCR = \frac{m_M}{m_{CL}} = \frac{\omega_M}{\omega_{CL}} \quad (\text{Eqn. 3})$$

In Eqn. 3, m_m is the mass of monomer and m_{cl} is the mass of crosslinker. An alternative way the relationship can be represented to gel purchasers is based on mass fractions, most commonly denoted by the lowercase variable omega with an appropriate subscript, but it is important to understand that the mass fractions are not representative of the entire solution in these cases. It is a special mass fraction that considers the total to be consisting only of the monomer and the crosslinker. These methods are most often employed in instructions for preparing the gel solutions for particular separations[14].

The MCR is a very important and powerful measure for PAGE gels because different ratios produce differently sized molecular sieves when coupled with variations in % T. A simplified way of viewing this concept is to compare the % T and % C equations. A stock solution can be made to have a constant % C, but by diluting the stock solution only the % T would undergo change in the monomer-crosslinker solution system—both would be diluted by the same factor in the new system they are placed. These methods have become so refined that only three MCRs are of major importance (1) 37.5:1, (2) 29:1, and (3) 19:1[15]. The % T is also well confined—not being less than 4 % T and almost never greater than 20 % T. Table 2 is a good summary of the various separations performed in these combinations of PAGE gels.

Isometric vs Gradient PAGE Gels

It is often the case that a researcher has a particular solution of proteins that will not adequately separate in what is best referred to as an isometric PAGE gel—a PAGE gel where only one size of molecular sieve is found continually throughout its matrix. In such cases, a gradient PAGE gel is employed. In the gradient gel, two solutions of reacting polymer are mixed at specific rates simultaneously as they are fed into a casting chamber. Once the gels have cured, the resulting PAGE gel has an accumulation of differently sized molecular sieves that are present throughout the length of the gel matrix. There are three types of gradient gels: (1) linear gradient, (2) concave exponential gradient, and (3) convex exponential gradient[16]. These different

types relate to how rapidly the change in molecular sieve size has occurred in the casting and curing process. The most commonly used gradient is the linear gradient. The experiments reported in this communication have explored this particular type of PAGE gel.

Gradient gels can experience unique problems with reproducibility when formed using available handcasting technologies. Handcasting these gels requires a special apparatus known as a “gradient former”. Most gradient formers are constructed of injection molded styrene and allow for various volumes of operation depending on the model. These devices range in cost from \$ 500 - \$ 1200 according to the retailer used for purchase. Bio-Rad is one such company that has the widest variety of PAGE gel equipment, supplies, and even pre-cast gel materials for purchase. They have defined kinetics for the gradient former in all its modes of operation but did not entirely explain how those could be derived[16,17,18,19].

The cost of these items and understanding their mechanisms of operation are all important considerations for researchers, especially in labs that are concerned with the operational budget use of such items may demand. One recent publication in the *Journal of Chemical Education* detailed a design for a graduate former using cheaper laboratory materials that proved to be just as effective as a commercial former[20]. Our studies have put that design to the test and have developed a model that can be used in simulations with MATLAB to predict the

<i>(% T, MRC)</i>	37.5:1	29:1	19:1
4 % T	-	-	100-1500 bp (native DNA/RNA) 70-500 bp (denatured DNA/RNA) 100-200 kD (protein)
5 % T	-	200-2000 bp (native DNA/RNA) 70-800 bp (denatured DNA/RNA)	-
6 % T	60-200 kD (protein)	> 150 kD (protein) 80-800 bp (native DNA/RNA) 50-500 bp (denatured DNA/RNA)	60-600 bp (native DNA/RNA) 40-400 bp (denatured DNA/RNA)
8 % T	50-150 kD (protein)	50-200 kD (protein) 60-400 bp (native DNA/RNA) 30-300 bp (denatured DNA/RNA)	40-150 kD (protein) 40-500 bp (native DNA/RNA) 20-200 bp (denatured DNA/RNA)
10 % T	25-100 kD (protein)	30-125 kD (protein) 50-300 bp (native DNA/RNA) 20-200 bp (denatured DNA/RNA)	20-100 kD (protein) 30-300 bp (native DNA/RNA) 15-150 bp (denatured DNA/RNA)
12 % T	15-80 kD (protein)	20-100 kD (protein) 40-200 bp (native DNA/RNA) 15-125 bp (denatured DNA/RNA)	15-70 kD (protein) 20-150 bp (native DNA/RNA) 10-100 bp (denatured DNA/RNA)
20 % T	-	10-70 kD (protein) < 40 bp (native DNA/RNA) < 40 bp (denatured DNA/RNA) < 30 kD (protein)	8-60 kD (protein)

Table 2. Separation Decision Matrix for PAGE Gels

gradient forming kinetics of these special PAGE gel materials.

Experimental Details

Materials

Acrylamide and bisacrylamide were purchased from Fisher Chemical. APS was purchased from Fisher Chemical and Bio-Rad. TEMED was purchased from Acros Organics and Bio-Rad. All water used in preparations was ASTM Grade I and obtained from a Millipore 3Q Water Purification unit. Tris base was purchased from Bio-Rad. L-Glycine was purchased from Bio-Rad. Kaleidoscope Pre-Stained Protein Standard was purchased from Bio-Rad. Nitrogen was purchased from Air Gas. Sodium dodecyl sulfate was purchased from Bio-Rad. Criterion Gel Electrophoresis Tank and Cassettes were purchased from Bio-Rad. PETG printing filaments were purchased from eSun. Silicon tubing, stopcocks and worm-gear hose clamps were purchased from US Plastics. Nylon barbed tubing connectors were purchased from McMaster-Carr. Silicon sealant and 3500 PSI-grade epoxy resin were purchased from Lowe's Home and Garden Store.

Polypropylene graduated cylinders and magnetic stir vanes were purchased from Fisher Scientific. Masterflex peristaltic pump tubing was purchased from Cole-Palmer. Circuitry components were purchased from Digi-Key and Amazon.com Marketplace.

Building the Gradient Former

The gradient former was constructed using a short rectangular base that was printed from

a 1.75 mm blue PETG filament with a Prusa i3 Model 3-D printer. Two polypropylene graduated cylinders with a total volume of 25-mL were then prepared by boring small holes at a point just above the base of their frames. One cylinder had two holes lined up in a straight line, whereas the other had only one hole bored into it. The cylinder with a single hole acted as the reservoir chamber and the cylinder with two holes acted as the mixing chamber of the apparatus.

The cylinders were then cemented to the PETG base using epoxy resin with a tensile rating of 3500 psi. After 30 minutes curing time, a Dremel tool was used to trim the larger end of a 1/4-inch to 3/16-in tubing connector leaving a thicker portion of the path between the two connections. Three of these outlets were made and then cemented into each of the holes using the resin and the thicker portion of the connectors. A small paper shim was used to keep the connectors level during the curing process. Once these pieces had fully cured (about one hour), they were gently tested by pulling on them with the researcher's hand to ensure there was no loose connection.

A silicone sealer was then used to coat the rim formed between the attached tubing connectors and the graduated cylinders. The layer was approximately 0.5 cm thick and encircled the nozzles fully. The sealer was then permitted to cure overnight for adequate waterproofing of the system. On the following day, several lengths of silicone tubing (3/16-in ID x 5/16-in OD) were cut with a pair of scissors to fit the gradient former. The first piece of tubing was

adjusted such that it connected the reservoir chamber to the mixing chamber without being much longer than the base each cylinder was attached and without having any kinks in the path of flow. A clamping-style paper clip was used to close flow between the chambers until the appropriate time. The second piece of tubing was cut into two pieces. One piece was short and served to connect the outlet of the mixing chamber to a 3-way valve that allowed good control of the flow of solutions out of the gradient former. The final piece of tubing was longer to allow for either gravimetric head to drive the system or enough room to connect a peristaltic pump in order to maintain good flow of the polymerizing solutions.

A micropipette tip for a 10 μ L pipet was used to secure to the end of the final tube in order to deliver the gel material directly to the casting chamber. The tip was secured using a 3/16-in sawtooth tube clamp with a locking screw. Water was then filled in each chamber to an equal height and the valves were fully opened in order to check flow characteristics and ensure there were no leaks in the system. A magnetic stir bar measuring 1-2 mm in diameter and about 1 cm in length was used to stir solutions in the gradient former during use. The size of this particular microscale stir bar was selected so that no impedance to flow was caused by the stir bar.

Casting operations involving the gradient former primarily took place under gravimetric conditions by placing the apparatus on stir plate that was placed on a

laboratory jack and elevated such that the discharge of the system was well below the chambers and able to flow easily into a prepared gel cassette. Figure 2 demonstrates an example of the setup using a picture of the apparatus. The total volume of gel solution prepared by the gradient former was 15 mL in each attempted polymerization.



Figure 2. Gradient Former Constructed for Experiments. Image of the constructed gradient former as it appears during an operation to cast a gradient gel.

Preparation of Solutions

A 250-mL 30 % T, 2.68 % C solution containing acrylamide and bisacrylamide was made using ASTM Grade I water, the monomer, and the cross-linker in a volumetric flask. The solution was decanted into a wide-mouth amber glass bottle and stored in the refrigerator until use. A 1.5 M Tris-HCl solution (pH = 8.8) was also prepared in a 250 mL volumetric flask and was decanted to amber wide-mouthed bottles for refrigerated storage between use. A 10% (w/v) APS solution was prepared daily during gelling experiments. The APS

solution serves as the radical initiator of the reaction.

Two gels were poured to test the gradient former. One gel was prepared as a standard separation gel with isometric sieves that had a stacking gel for the first 1 cm of gel length. A stacking gel is a 4 % T PAGE gel with a more acidic buffer in its matrix that helps line-up proteins before they travel through the resolving gel. The other solutions were used in the gradient former to produce a linear gradient ranging from 4 % T to 20 % T.

Gel Casting

In these preparations, the APS solutions should always be fresh and the TEMED should always be added just before time to start polymerization. Table 3 details the volumes of each component necessary to prepare the gel solutions for both types of gels in the study. Once all solutions were admixed and it was time to begin a polymerization, the amount of APS and TEMED required for the gel were added and then the 50-mL centrifuge tube used to mix the solution was capped and inverted several

times to mix the substances thoroughly. A 1000 μ L pipet was then used to transfer the media into the casting chamber (12 % T gels with a 4 % T stacking gel) or the solution was poured from the centrifuge tube into the graduated cylinder of the appropriate type on the gradient former. The gel cassettes used for casting were designed to fit the Bio-Rad Criterion Electrophoresis Unit (a midi-sized gel electrophoresis unit).

During casting, the tip at the end of the outlet was inserted in the gel plate and the stirrer was set to 20 % power. The paper clip was then released from the tube connecting the reservoir tank and the mixing tank, and then the three-way valve was opened to allow the solution to flow into the gel cassette. Once solution was dispensed the gel was left standing with a comb inserted for 45 minutes until gelation had occurred. The gradient former was rinsed thoroughly after each use with deionized water, followed by a mildalconox wash and further rinse with water. A new tip was used for any subsequent gel castings as these are disposable consumables.

	4-SG	12-RG	4-GS	20-GS
Acrylamide-Bisacrylamide Stock (30 % T, 2.68 % C)	1.00 mL	6.00 mL	1.00 mL	5.00 mL
0.5 M Tris-HCl Buffer (pH = 6.8)	3.75 mL	-	-	-
1.5 M Tris-HCl Buffer (pH = 8.8)	-	3.75 mL	1.88 mL	1.88 mL
10 % (w/v) SDS	150 μ L	150 μ L	-	-
Glycerol	-	3.00 mL	-	425 μ L
ASTM Grade I Water	9.00 mL	2.00 mL	4.62 mL	200 μ L
10 % (w/v) APS	75 μ L	75 μ L	37.5 μ L	37.5 μ L
TEMED	7.5 μ L	7.5 μ L	3.75 μ L	3.75 μ L

Table 3. Formulations for PAGE Gels in Experiments

Materials Testing

The cast gels were placed in the electrophoresis unit and bathed in 1X Tris-Glycine Running Buffer at pH 8.6. A gel loading tip and micropipette were used to deliver 10 μ L of Bio-Rad Pre-Stained Kaleidoscope Protein Plus standard into gel wells no. 2 and no. 8 of the cassette. The chamber was then sealed, and electrophoresis was carried out for 45 minutes at a constant voltage of 250 VDC. The gels were then photographed using a high-definition camera and a light board after the residual buffer was rinsed from them with deionized water.

Designing and Building an Affordable Peristaltic Pump

The peristaltic pump chosen for use with this project was developed from an open source Thingiverse file designed to create four identical peristaltic pump casings, as well as a frame using available 3-D printing technologies for thermoplastics (e.g. Raise N2, MakerBot, Ultimaker)[21]. The parts were printed from a PETG filament using the designers recommended settings. Ball bearings, motors, motor drivers, and the Arduino components were then assembled and optimized. The most arduous of these tasks was the optimization of the electrical components and the integration of software for chosen functioning.

The particular components selected for this project designed the pump in a way where it uses a rotary encoder (a more analog I/O device) to control the speed of the stepper

motor driving the pump. It was this component that required the most optimization between software components as most components use digital signals directly, and the encoder required a pattern of interrupt sequencing in order to function well with the apparatus. The prototype pump was connected through a series of perfboards to which circuitry components were soldered directly. The pump was field tested with the gradient former to ensure that the average bucket volumetric flowrate was consistent with recommended gradient formation parameters.

Developing the MATLAB Simulation for Gradient Former Kinetics

The model used to generate predictions of kinetics in the gradient former was based on information provided by the Bio-Rad manuals on gradient formers where a kinetic model has been presented. The model was taken and then incorporated with fluid dynamics equations derived directly from Bernoulli's Principle since the system is driven in many cases by a gravimetric head. The ode15s function solver was selected for this purpose since the system is not at steady state and cannot be modeled in such a case. These parameters allowed for instantaneous predictions of the concentration profile. For a lack of data in the specific case, a k-value of 1 was assumed for all k-values in order to test the model. Estimations were selected to account for changes in molecular weight and viscosity as the reaction progresses in solution.

Results

Isometric and Gradient Gels

Photographic results (Figure 3) were compared to each other and to the Bio-Rad manual on protein standards that displays expected results for the Kaleidoscope Pre-Stained Standard. The standard is formulated to produce 10 colored bands that alternate in colors of blue, violet, pink, green, and yellow. The molecular weight range of the standard is from 10 kD to 250 kD. The particular standard provides at least 94 % accuracy in weight estimation when used in a 4-20% Tris-HCl gel[22]. Thus, not all bands can separate in a non-gradient gel. The gradient gel produced with the gradient former demonstrated equivalent results for the standard in both lanes of travel that compared to the manufacturer's performance standard. The standard run in

the 12 % T, 2.68 % C gel with the stacking gel of 4 % T, 2.68 % C did not allow full separation of all proteins in the standard. These results were consistent with those expected for a good result.

MATLAB Simulation

The results of the MATLAB simulation demonstrated a similar picture for linear gradients to that described in Bio-Rad manuals on gradient formers, but there are some slight inflections in this beginning model due to a lack of information in some kinetic parameters and the fact that it is compared on the basis of time-dependence as opposed to volume-dependence. Further work must be done with the model to have it produce a curve for exponential gradients. In Figure 4, the resultant model and the linear model more similar to the literature are compared.

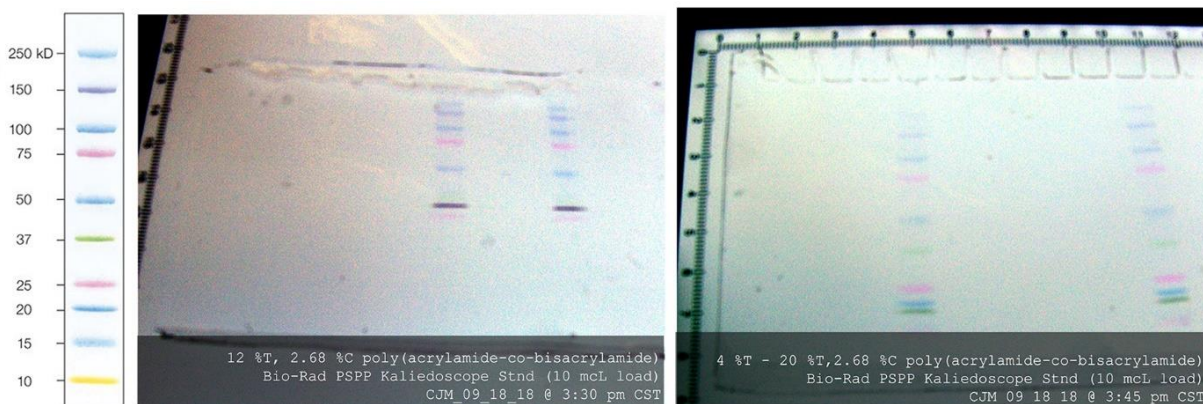


Figure 3. Comparison of the Isometric Gel and Gradient Gel. Bio-Rad Protein Plus Pre-Stained Kaleidoscope Standard Ladder (left) is compared against the image of the isometric PAGE gel separation of the same (middle) and the 4-20% Tris-HCl Gradient Gel (right). The gradient gel had separation similar to the manufacturer's specifications for this protein standard. A collection of protein bands accumulated in the final appearing band of the isometric gel—demonstrating that the bands cannot fully separate without the use of the gradient.

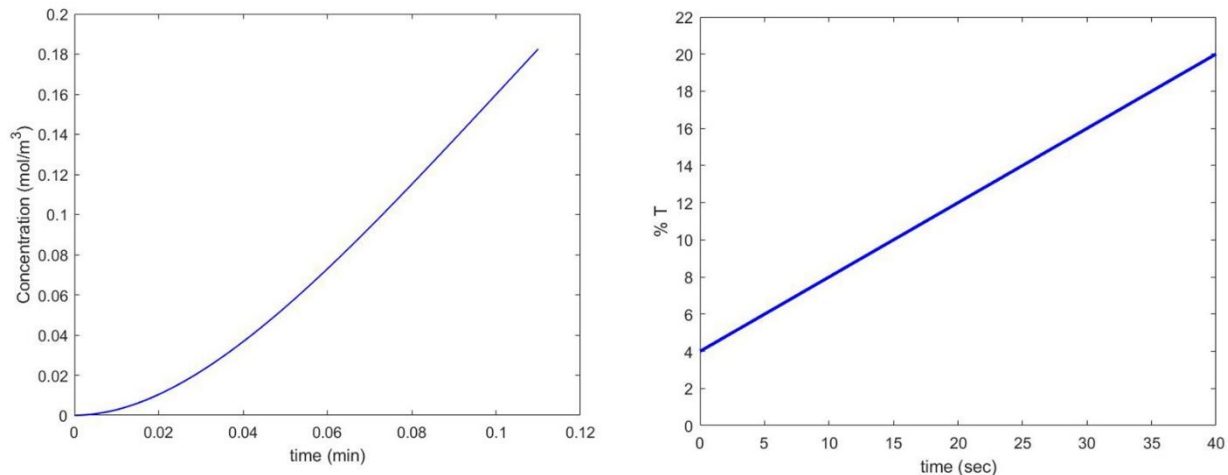


Figure 4. Comparison of Simulated Model and Reported Models. Model of polymer concentration as a function of time in a linear gradient former configuration (left) is compared against the linear gradient former as a function of time in the Bio-Rad models (right). The average trend holds true for the modeled former but is different due to a focus on concentration as opposed to % T and differences in the time vs volumetric comparisons.

Discussion

Isometric and Gradient Gels

The results obtained regarding the different PAGE gels in this series of testing was consistent with expected results. The pore-size of the hydrogels have been well-studied and defined over the past few decades and tables can be readily accessed that predict molecular weight correlation as a function of length for various configurations of the gels. In the case of these experiments, we are modeling the formation of the materials and demonstrating that the more affordable gradient former designs produce results as expected with protein standards. Several reasons pertain to that choice: (1) the various colors in the standard make photographic visualization of the separation easier, (2) standards are prepared in a way that concentrations and ingredients are documented carefully, and quality controlled by the manufacturers, and (3) the questions posed by this project do not pertain to

specific protein separations that may be problematic for the gel material at this time. For those reasons, the protein standard makes a good test solution for the material to separate as it can verify the working condition of the equipment and the functionality of the gel.

The standard used in this case is only adequate for estimating protein weight to a power of 94 %, and the unstained version of this standard is necessary for estimation greater than 95 % [22]. The standard was a good choice in this case because it requires the selected gradient of production in order to fully separate in the same manner as documented by its manufacturer. Future work with the gradient former will analyze how varying these concentrations in the gel may require the use of specific standards in materials testing, and some protein samples will also be tested in these gels to see if it performs adequately for experimental samples.

The Peristaltic Pump

The peristaltic pump designed for this gradient former performed adequately to the standards required in the Bio-Rad manual for formation of gradients. The recommendation is that all fluid should be extracted from the gradient former within 8-10 minutes of the time polymerization begins (the moment when TEMED has been added in the presence of APS)[16]. Future work with this device will include developing an additively manufactured casing for the components that makes it efficient for the use of lab space. Estimations of the cost in producing the pump are less than \$ 70. A price that is vastly different from the market for peristaltic pumps sold commercially (typically \$ 800 - \$ 2500).

MATLAB Simulation

The MATLAB script generated for the project was developed by first looking at the applicable laws that govern the fluid dynamics and chemical kinetics of the process. These two areas are combined in the final model along with certain rheological properties of the solutions that tend to undergo change during polymerization. There are four major components to the simulation: (1) Bernoulli's Principle, (2) Macroscopic Fluid Balance, (3) Reactor Material Balance, and (4) molecular weight-based changes in solution (e.g. viscosity, density).

The fluid dynamics of the gradient former were the first to be considered in the

development of our model. These were simulated by combining Bernoulli's Principle (Eqn. 4) with the Macroscopic Fluid Balance (Eqn. 5).

$$P_1 + \rho_1 g h_1 + \frac{1}{2} \rho_1 v_1^2 = P_2 + \rho_2 g h_2 + \frac{1}{2} \rho_2 v_2^2 \quad (\text{Eqn. 4})$$

In Eqn. 4, P_1 is the stagnant pressure of sub-system 1, ρ_1 is the density of the fluid in sub-system 1, g is the acceleration due to gravity, h_1 is the height of the fluid in sub-system 1, v_1 is the average velocity of the fluid in sub-system 1, P_2 is the stagnant pressure of sub-system 2, ρ_2 is the density of the fluid in sub-system 2, h_2 is the height of the fluid in sub-system 2, and v_2 is the average velocity of the fluid in sub-system 2. Bernoulli's Principle relates the stagnant pressure, static pressure, and dynamic pressure of one subsystem to a second subsystem when the two are connected.

In Eqn. 5, ρ is the density of the fluid considered in the equation, V is the volume, v is the velocity, N is the normal of the direction of the velocity, and A is the cross-sectional area. Essentially, this equation is the macroscopic fluid balance that says mass traveling as a fluid must be equal to the volume in the system as a product of the average density. The volume is the control volume and is composed of the volumetric flow entering, exiting, and occurring at the interfaces. The volume is given by the integral of the cross-sectional area and the product of the velocity from the fluid streamlines.

$$\frac{d}{dt} \left\{ \rho \int_{V(t)} dV = \rho \left[\int_{A(t),enter} (\vec{v} \cdot \vec{N}) dA - \int_{A(t),exit} (\vec{v} \cdot \vec{N}) dA - \int_{A(t),interface} (\vec{v} \cdot \vec{N}) dA \right] \right\} \quad (\text{Eqn. 5})$$

In order to use this specific portion of the model, steady-state had to be assumed regarding the flow of fluids. The assumption in this case produced a good prediction of results, but it is still an approximation because the material flowing is a constantly reacting material at the time it passes through the system. These particular kinds of reactions tend to produce volumetric contractions due to volume changes from reaction[23]. The equations could later be substituted from reactor models that included thermodynamic data that allows for a more accurate prediction of those volume changes. Notwithstanding, the fluid balance is really only one portion of the larger picture.

The material balance (Eqn. 6) is the more important of the two considerations in this case because it includes kinetic information about the reaction as it occurs instantaneously.

$$\frac{d}{dt} \int_V c_j dV = Q_f c_{j_f} - Q_1 c_{j_1} + \int_V R_j dV \quad (\text{Eqn. 6})$$

In Eqn. 6, c_j is the concentration of the species j , Q_f is the volumetric flow rate of the feed stream, c_{j_f} is the concentration of species j in the feed stream, Q_1 is the exiting volumetric flow rate, c_{j_1} is the concentration of species j in the exit stream, and R_j is the reaction rate of species j . The resulting integration produces a differential equation for each species in the system that relates the molar composition to the reacting volume (V_R or ΔV).

The material balance includes information such as the volumetric flow rate (driven by Bernoulli's Principle), and the initial concentrations at the time the reaction is initiated. Certain assumptions have to be made for the model to function, but those assumptions must primarily be based on the crosslinking reaction as opposed to the parallel reaction of the chain extensions that occur due to the monomer present in solution. For that reason, the general quasi-steady state solutions for reaction kinetics of free radical polymerizations do not specifically hold true. Those laws primarily pertain to linear polymerizations where only the monomer contributes to the overall process. The assumption of a first-order irreversible reaction made a similar prediction to the relationships communicated in Bio-Rad manuals, but this was developed as if for a single reaction.

The picture in such case is an incomplete one because in a free radical polymerization there are several reactions which occur that include (1) initiation, (2) activation, (3) propagation, and (4) termination. In the instance of propagation for this reaction there are two parallel reactions that are occurring. The first reaction is one in which only the monomer is reacting on sites similar to the monomer resulting in chain extensions of the matrix. The second reaction is one in which the crosslinker combines with four strands in solution to crosslink two linear units into a crosslinked node. The former reaction has been well studied in different solution systems and the reaction rate constants that are used with the standard quasi-steady state rate law for

polymerization of this type (Eqn. 7) have been documented[24]. The latter reaction of the two has been studied in the context of catalyst differences, concentration differences, and temperature differences; however, those studies used less accurate measurement techniques that could not correlate directly to a concentration in the solution and they did not attempt to find a mathematical model that could determine a k-value for the reaction[25,26,27]. Thus, the crosslinking reaction is not well studied or defined in terms of making predictions with regard to the reaction.

$$R_p = k_p \left(\frac{fk_d [I]}{k_t} \right)^{0.5} [M] \quad (\text{Eqn. 7})$$

In Eqn. 7, k_p is the rate constant of the reaction for propagation, f is the fraction of dissociated initiator that produces radicals for propagation, k_d is the rate constant of disassociation of the initiator into radicals, k_t is the rate constant of termination of radicals, $[I]$ is the concentration of initiator in solution, and $[M]$ is the concentration of monomer in solution.

Lastly, it is important to understand that as a polymer reacts the molecular weight distribution in the solution is actively changing. These changes lead to viscosity changes in the solution which could be modeled using a power law relationship employed as a tool in rheology to predict the effect particular molecular weights have on the viscosity of a single species, but for such as estimation to hold true the average of those molecular weights and viscosities

would need to be measured to find that pattern[24]. The prediction would also have to be made for the particular case in question since any literature values often exclude the crosslinking reaction and have been determined only for forming poly(acrylamide). For the simulation, a constant value was chosen for the initial solution and an alternative constant was used to reflect the direction of the change the trend would undergo. These were values between 0 and 1. Future work may examine if a power law can be found that could be used in the model to more accurately portray that aspect of the system.

Conclusion

Gels

The gradient former built using the guidelines of the *Journal of Chemical Education* paper worked well for producing gradients in our studies. We would emphasize the importance that the diameter of the outlets should be uniform since alterations can result in pressure differences as predicted by our fluids model and observed in an initial test of the former. The problem was resolved by widening the diameter of a particular outlet that had been deformed due to melting of the polymer during use of the tool. For pouring only a smaller size of gel, such as the mini-formats or midi-formats, the gradient former built would be an excellent tool for a biochemistry lab. Most commercial formers are designed for large format systems and have volumetric capacities that far exceed the volume for a single midi-size gel.

Pump

A peristaltic pump is not particularly necessary for a gradient former unless a jack or other method to increase elevation of the tank relative to the outflow tract is not available. It may also be the case that it is less convenient to use the elevation tools due to space in the laboratory at such time. In those circumstances, the use of a small peristaltic pump is ideal. The head of the pump should not be so high that an exceptionally high flow rate is required to maintain function of the pump (a problem with some commercial units), and the model built is not capable of producing such a head—making it ideal for this application. The pump is also a bargain price compared to purchasing a more robust pump that would in its minimum price range be eight times the cost of building this small, yet functional, unit.

MATLAB Simulation

Most future work with this particular project will focus on developing a well defined kinetic model for the crosslinking reaction that occurs in the formation of the gel. Dynamic Mechanical Analysis is a method for kinetics in such materials using a complex rheometer[28]. Some pilot experiments have been undertaken on an AR500 Rheometer by TA Instruments that demonstrate the cross-linking reaction regresses well using a Chapman-Richards Growth Function to model the kinetics of the reaction. It has been possible to determine k-values and derivatives from the regressions made in this way by applying a Mooney-Rivlin type treatment that relates the storage modulus of the gel material to

the crosslink density[29]. Further work may look at how a power law relationship may be used to predict changes in viscosity that occur in the solution, and those relationships may then be added to a more informed dynamic simulation.

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References

1. Bio-Rad. *2-D Electrophoresis Workflow How-To Guide*, 4th ed.; Bio-Rad Laboratories, Inc.: Hercules, CA, 2013.
2. ThermoFisher Scientific. *Protein Gel Electrophoresis Technical Handbook*; ThermoFisher Scientific, Inc., 2016.

3. Wagle, D. Agarose Gel Electrophoresis. Presentation. Cookeville, TN, USA 2018.
4. Thompson, J. W.; Stretz, H. A.; Arce, P. E. Preliminary Observations of the Role of Material Morphology on Protein-Electrophoretic Transport in Gold Nanocomposite Hydrogels. *Ind. Eng. Chem. Res.* **2010**, *49* (23), 12104–12110.
5. Thompson, J. W.; Stretz, H. A.; Arce, P. E. Thermoresponsive Microparticle Composite Hydrogels for Electrophoresis. US 2009/0127116 A1, 2009.
6. Thompson, J. W.; Stretz, H. A.; Arce, P. E.; Gao, H.; Ploehn, H. J.; He, J. Effect of Magnetization on the Gel Structure and Protein Electrophoresis in Polyacrylamide Hydrogel Nanocomposites. *J. Appl. Polym. Sci.* **2012**, *126*, 1600–1612.
7. Dorfman, K. D.; King, S. B.; Olson, D. W.; Thomas, J. D. P.; Tree, D. R. Beyond Gel Electrophoresis: Microfluidic Separations, Fluorescence Burst Analysis, and DNA Stretching. *Chem. Rev.* **2013**, *113* (4), 2584–2667.
8. Boles, J.; Weintraub, S. Personal Interviews. 2018.
9. IUPAC. A Brief Guide to Polymer Nomenclature (Version 1.1). *Pure Appl. Chem.* **2012**, *84*, 2167–2169.
10. IUPAC Polymer Division. *Compendium of Polymer Terminology and Nomenclature: IUPAC Recommendations 2008*; Jones, R. J., Kahovec, J., Stepto, R., Wilks, E. S., Hess, M., Kitayama, T., Metanovski, W. V., Jenkins, A., Kratochvil, P., Eds.; The Royal Society of Chemistry: Cambridge, UK, 2009.
11. Lin, H. R. Solution Polymerization of Acrylamide Using Potassium Persulfate as an Initiator: Kinetic Studies, Temperature and PH Dependence. *Eur. Polym. J.* **2001**, *37* (7), 1507–1510.
12. Menter, P. Acrylamide Polymerization—A Practical Approach. *Bio-Rad Tech Note* **2000**, No. 1156, 1–8.
13. Thompson, J. W. Role of Material Morphology on Separation of Proteins in Nanocomposite Hydrogels, Tennessee Technological University, 2012.
14. Interchim. Acrylamide 40 % Solutions. <http://www.interchim.com/catalogue/469/gels-acrylamides-agaroses.html> (accessed May 31, 2018).
15. Unknown. The Polyacrylamide Matrix <https://www.nationaldiagnostics.com/electrophoresis/article/polyacrylamide-matrix> (accessed Oct 6, 2018).
16. Bio-Rad Life Sciences Group. *Model 385 and 395 Gradient Former Instruction Manual*, C.; Bio-Rad Laboratories, Inc.: Hercules, CA, 2001.

17. Bio-Rad Life Science Group. *Model 475 Gradient Delivery System Instruction Manual*, B.; Bio-Rad Laboratories, Inc.: Hercules, CA, 2011.
18. Bio-Rad Life Science Group. *Model 495 Gradient Former Instruction Manual*; Bio-Rad Laboratories, Inc.: Hercules, CA, 2011.
19. Bio-Rad Life Science Group. *Model 485 Gradient Former Instruction Manual Catalog Number*, A.; Bio-Rad Laboratories, Inc.: Hercules, CA, 2011.
20. Flurkey, W. H. An Inexpensive Gradient Maker for the Biochemistry Laboratory. *J. Chem. Educ.* **2000**, *77* (8), 1041.
21. Silisand. Peristaltic Pump Improved for Nema 17 - Thingiverse
<https://www.thingiverse.com/thing:1134817> (accessed May 31, 2018).
22. BioRad Life Sciences Group. *Precision Plus Protein Kaleidoscope Standards Instruction Manual*, G.; Bio-Rad Laboratories, Inc.: Hercules, CA, 2016.
23. Rawlings, J. B.; Ekerdt, J. G. *Chemical Reactor Analysis and Design Fundamentals*, 2nd ed.; Nob Hill Publishing: Madison, Wisconsin, 2013.
24. Flory, P. J. Polymerization of Unsaturated Monomers by Free Radical Mechanisms. In *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1971; pp 106–177.
25. Gelfi, C.; Righetti, P. G. Polymerization Kinetics of Polyacrylamide Gels I. Effect of Different Cross-Linkers. *Electrophoresis* **1981**, *2* (4), 213–219.
26. Gelfi, C.; Righetti, P. G. Polymerization Kinetics of Polyacrylamide Gels II. Effect of Temperature. *Electrophoresis* **1981**, *2* (4), 220–228.
27. Righetti, P. G.; Gelfi, C.; Bosisio, A. B. Polymerization Kinetics of Polyacrylamide Gels. III. Effect of Catalysts. *Electrophoresis* **1981**, *2* (5–6), 291–295.
28. Mendoza Puente CI, Avalos Belmontes F, Ramos deValle LF, O. C. J. Chemical Reaction Kinetics through Dynamic Mechanical Analysis Data. *MOJ Polym. Sci.* **2017**, *1* (3), 109–111.
29. Xia, Z.; Patchan, M.; Maranchi, J.; Elisseeff, J.; Trexler, M. Determination of Crosslinking Density of Hydrogels Prepared from Microcrystalline Cellulose. *J. Appl. Polym. Sci.* **2013**, 4537–4541.

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