Synthesis, Characterization, Processing and Physical Behavior of Melt-Processible Acrylonitrile Co- and Terpolymers for Carbon Fibers: Effect of Synthetic Variables on Copolymer Structure

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(ABSTRACT)

A novel photocrosslinkable and melt processible terpolymer precursor for carbon fibers has been successfully synthesized and characterized. The terpolymer was synthesized by an efficient emulsion polymerization route and has a typical composition of acrylonitrile/ methyl acrylate/acryloyl benzophenone in the molar ratio of 85/14/1. This thesis describes a systematic variation of the polymerization variables in the emulsion polymerization which may further enhance the system. In particular, the effects of chain transfer agent, initiator, and surfactant concentration on the polymer properties were studied.

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Chapter I: Introduction

Both natural and man-made fibers have had a significant impact on our way of life. Throughout time man has been linked with natural fibers, and the introduction of acrylic fibers by DuPont in 1944 had a dynamic effect on the rest of society. However, the monomer from which acrylic fibers originate was first made in 1893 in Germany, and was used by DuPont in other applications. Acrylic fibers have evolved to become very important to the textile industry. The basic polymer used for acrylic fibers is polyacrylonitrile,[1] which is also known by a host of trade names, including Biofresh, Creslan, and Duraspun. Presently these fibers have a commercial volume of about six billion pounds annually. Polyacrylonitrile has also been transformed into carbon fibers, with a production of about thirty million pounds. The duel role for acrylic/carbon fiber only exists because of the complex nature of the thermal process necessary to produce carbon fiber. Processing of carbon fiber may, in principle, be explored via two routes - solution or melt processing. The melt processing is the more complicated of the two methods, but would be more environmentally friendly. This method requires the addition of a comonomer to lower the crystalline melting point (T_m) below the decomposition temperature of 300 ºC. Lowering the crystalline melting point could allow the fiber to be melt processed. The melt processing of the co- or terpolymer fiber occurs at 220 ºC, which is more than 100 ºC above the glass transition temperature (T_g), while still yielding sturdy fibers. This gives rise to a more environmentally desirable processing method.

The objective of this research was to develop a method of melt processing this polymer with adequate stability while maintaining strength. To study the synthetic variables (chain

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[1] Tirrell, D. A. *Copolymerization*. In *Encyclopedia of Polymer Science and Engineering;* Mark, H. F.; Bikales, N. M.; Overberger, C. G.; Menges, G. Eds.; Wiley-Interscience: New York, 1986; Vol. 4; pp. 192-233.

transfer agent, initiator, surfactant) that may enhance the synthesis and molecular weight. This research also studied the effect of the addition of a termonomer - acryloyl benzophnone (ABP) - on melt processability. This research studied how emulsion polymerization can be affected with chain transfer agent (1-dodecanethiol, DOSH), initiatior (ammonium persulfate, APS), and surfactant (Dow-Fax, sodium lauryl sulfate). The comonomers used were acrylonitrile (AN) and methyl acrylate (MA), at AN compositions of 85% or less, which allows the melting point to be significantly reduced. Several characterization techniques and instruments were employed, which will be discussed further in the Experimental section.

Chapter II. Literature Review

Acrylic Textiles Fiber History

For thousands of years, man was limited to the use of natural fibers that could be fabricated from what the environment had to offer. However, man devised a way to create fibers from his surroundings. The wool from sheep was used to make fibers for clothes, but wool fiber was irritating to the touch, and was eaten by moths. Sheep's wool was not very comfortable (imagine wool under garments), so cotton and linen fabrics were developed for use in clothing, but they would wrinkle from wear and washing. Silk was discovered next, but it was very delicate, expensive, and required many silk worms to retrieve the necessary silk thread to create fiber. About a century ago Rayon, a cellulose-based manufactured fiber, was introduced to the field of fiber chemistry.[2]

Fiber engineers can combine, modify and tailor fibers in ways far beyond the performance limits of fiber drawn from the silkworm cocoon, grown in the fields, or spun from animal wool. Some of the first attempts to create artificial fiber were introduced as early as 1664. Robert Hooke thought that he could produce a fiber that was better than silk. This was a grand idea for the period, and it was never realized until two hundred years later. The first patent for artificial silk was given to a Swiss chemist named Audemars. He dissolved the cambium layer of the mulberry tree, and chemically modified it to yield cellulose. He formed threads but did not extrude the cellulosic liquid through a small hole like the silk worm. In the late 1800s, Sir Joseph W. Swan experimented with forcing a liquid through a fine hole into a coagulating bath. This could also be used to make textiles. In 1885 Swan's wife crocheted the fibers and exhibited them in London.

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[2] Masson Jomes, C. *Acrylic Fiber Technology and Application.* Marcel Dekker, Inc.; New York, New York, 1995; pp 3-368.

The first commercial-scale production of a manufactured fiber was achieved by French chemist Count Hilaire de Chardonnet in1889; his fabrics of “artificial silk” caused a sensation at the Paris Exhibition. Two years later he built the first commercial rayon plant at Besancon, France, and was known as the father of the rayon industry. Although the rayon industry was the interest of the day it was not commercially useful until the 1900s. An American by the name of Samuel Courtaulds formed a company named American Viscose Company, which produced rayon in 1910.

The film industry owes a bit of gratitude to the development of acetate, which was another cellulosic derivative. By 1910, Camille and Henry Dreyfus were making acetate motion picture film in Basel, Switzerland. During World War I, they built a plant in England to produce cellulose acetate dope for airplane wings. During the first world war, the United States propositioned the Dreyfus brothers to build a plant in Maryland to make their product for American warplanes. The Celanese Company developed the first commercial textile uses for acetate in fiber form in 1924. In the mid 1920s the demand for rayon was increasing and could be purchased for half the price of raw silk. The American fiber industry grew rapidly to nearly 70% of the national market by the last decade of the century.

The introduction of polyamides or nylon sparked a new era of fiber and its uses. The scientist leading the charge was Wallace Carothers. In 1931, while at DuPont, his research focused on large molecules called polymers. The polymer of interest was known as “66,” a number derived from its molecular structure, which has six carbons from the acid and six carbons from the amine components. Nylon’s arrival produced a revolution in the fiber industry.[2] Unlike rayon and acetate, which are developed from plant cellulose, nylon was synthesized completely from petrochemicals. Nylon spawned a completely new world of manufactured fibers. DuPont started commercial production of nylon in 1939. Some of its pioneering efforts were in testing nylons in parachute fabric and women's stockings. Women were ecstatic about the new material; however, this was short lived. Due to World War II, the nylon hose, which sold for $1.25 a pair before the war, moved in the black market at $10 a pair. Betty Grable, a movie star of the era, helped drive the price of nylons to a price of 40,000 at auction to promote the war effort.

During the War, nylon replaced Asian silk in parachutes. It also found uses in tires, tents, ropes, ponchos, and other military supplies, and even was used in the production of a high-grade paper for U.S. currency. At the outset of the War, cotton accounted for more than 80% of all fibers used. Manufactured and wool fibers shared the remaining 20%. By the end of the War in August 1945, cotton stood at 75% of the fiber market. Synthetic polymeric fibers had risen to 25%.

At the end of the war America entered a period of economic growth driven by conversion of nylon production to civilian uses, one of which was ladies' stockings. By the end of the 1940s, nylon was being used in carpeting and automobile upholstery. At the same time, three new generic manufactured fibers started production. Dow Badische Company (today, BASF Corporation) introduced metalized fibers; Union Carbide Corporation developed modacrylic fiber; and Hercules, Inc. added olefin fiber.

By the 1950s, the fiber industry was in full swing supplying more than 20% of the fiber needs of textile mills. Acrylic fibers based on acrylonitrile copolymers were added to the list of generic names, as DuPont started production of this wool-like product.

J.T. Dickson and J. R. Whinfield, who produced a polyester fiber by condensation polymerization of ethylene glycol with terephthalic acid, revisited Wallace Carothers' early research. DuPont chemical company wisely acquired the patent rights.

During the summer of 1952, the phrase "wash and wear" was coined to describe a new blend of cotton and acrylic. The term eventually was applied to a wide variety of manufactured fiber blends. Commercial production of polyester fiber transformed the "wash and wear" novelty into a revolution in textile product and performance. Polyesters reached the apex of commercialization in 1953. The discovery of new fiber chemistries has decreased in recent years, and fiber engineers have focused their attention on improving the physical and mechanical properties of fibers.

During the 1960s and 1970s, consumption of polyester clothing increased dramatically. Electric dryers replaced clotheslines, and the "wash and wear" garments became even more attractive. Fabrics became more durable and required less maintenance, and colors became more permanent. New dyeing effects were being achieved and shape-retaining knits offered new comfort and style.

The use of fibers was spurred on by continuous innovation and modification. The revolutionary new fibers were modified to offer greater comfort, provide flame resistance, reduce clinging, release soil, and achieve greater whiteness, special dullness or luster, easier dyeability, and better blending qualities. New fiber shapes and thicknesses were introduced to meet special needs. Spandex, a stretchable fiber aramid, a high-temperature-resistant polyamide and para-aramid, with exceptional strength-to-weight properties, was introduced into the marketplace. Manufactured fibers received renewed attention with the onset of the U.S. space program. The industry provided special fibers for uses ranging from clothing for the astronauts to spaceship nose cones. In 1969 Neil Armstrong took “one small step for man, one giant leap for mankind.” His lunar space suit included multi-layers of nylon and aramid fabrics. The flag he placed on the moon was made of nylon!

Today, the exhaust nozzles of the two large booster rockets that elevate the space shuttle into orbit contain 30,000 pounds of carbonized rayon. Carbon fiber composites are used as structural components in the latest commercial aircraft, adding strength and lowering weight and fuel costs.[2] The use of some of these high-performance materials is a part of the web of discovery.

During the early 1970s, consumer demand for safety products increased. Although acrylic materials made nice clothes and pajamas, they were not flame retardant. This need for flame retardant materials for children’s clothes was tackled by the manufactured fiber industry with a 20 million dollar investment in the development of flame-retardant fibers. The federal government expanded its mandate to include that carpets in homes be flame retardant as well. Once again the fiber industry was up to the challenge and developed flammability standards for carpets. Today in the U.S. carpet market, 99% of all surface fibers are now manufactured fibers.

In late 1973 the Nation was hit by a shortage of petroleum. In response, the fiber industry reduced their energy requirements to produce a pound of fiber by 26%. By then, the industry was using only 1% of the Nation's petroleum supply to provide two-thirds of all fibers used by American textile mills.

Originality is one defining feature of the manufactured fiber industry. Man-made fibers today are more bountiful and diverse than any found in nature. Materials are now consistently created in the fiber industry's laboratories.

Nylon variations are used to produce carpets that can be cleaned easily even after they have been stained. Segmented urea-urethanes, such as Spandex™ are machine washable and pseudo-silk polyester occupies a solid place in the U.S. apparel market. Some microfibers have been instrumental in remaking the world of fashion.

The Federal Trade Commission decided to classify modacrylic and acrylic fibers into two categories. Although these fibers are close in composition, there are small differences that differentiate them. A modacrylic fiber is defined as a manufactured fiber in which the fiber-forming substance is any long chain synthetic polymer composed of less than 85% but at least 35% by weight of acrylontitrile units.

Modacrylics are vinyl chloride-acrylonitrile copolymers that have better heat retention. Acrylic fibers are stronger than modacrylic fibers, but modacrylics are more durable. The reason that modacrylics are so appealing to the public is their softness, resiliency, color fastness, abrasion resistance, flame resistance, and shape retention. These fibers feel light and have good insulating qualities. Modacrylic fabrics have good dimensional stability and retain their shape, but shrinkage can occur because of their sensitivity to heat. However, modacrylics have a long lifetime because they are not sensitive to light, moths, mildew, and age. These fibers are self-extinguishing, which makes them excellent candidates for children’s sleepwear and commercial draperies.

Modacrylic and acrylic fibers can be processed by two methods. One method is wet spinning, which occurs when a polymer is dissolved in a solvent and the solution is extruded into a chemical bath. The dry spinning method involves coagulation of a fiber as solvent evaporates.

These processing methods have contributed to the widespread use of modacrylic fibers. The dry spinning method was introduced by DuPont using dimethyl formamide (DMF) as the solvent and methyl methacrylate as the dye modifier. The wet spinning process was commercialized by Chemstrand and involved the use of dimethyl acetamide as the solvent and vinyl acetate as the dye modifier. The wet-spinning process used by Courtaulds introduced aqueous sodium thiocyanate and methyl methacrylate as the dye site modifier.

I.G. Farben has developed solvents for polyacrylonitrile which have led to the development of wet and dry spinning processes for making fibers.[3] This company was well known in Germany and was responsible for the development of several other companies' acrylic fibers, such as Bayer's Dralon, Hoecht's Dolan, etc. Throughout the world, some parts were producing 800 million pounds per year while other parts of the world were producing in excess of 1.4 billion pounds per year. Fiber research and production assisted countries with a large labor force in providing employment because of the high demand for acrylic or modacrylic fibers. During 1990 there were 68 plants worldwide producing 5.1 billions pounds of acrylic and modacrylic fibers.

In recent years, some companies have stopped fiber production due to an excess of acrylic fiber. There has been a resurgence of cotton fiber for clothing. However, acrylic fibers have benefits such as the ability to wick moisture without absorbing it, which is a good quality for use in athletic socks and shirts. The fiber even has some antimicrobial benefits, which was discovered in 1987.[4] Acrylic fiber is known to be the best precursor fiber for the development of carbon fiber, which will be discussed in greater detail later in the paper.

In many cases, acrylic fiber is desirable to the end user because of its ability to absorb moisture without making the skin feel damp. Acrylic fiber can accomplish this by wicking the moisture away from the body and transporting it to the surface of the garment where it can be

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[3] Rein, H.,*Survey of Synthetic Fiber Developmen,* Angew Chem, 1948 Vol. 60. pp. 159-161
[4] Pardini, S. P., to Du Pont, U.S. Patent 4,708,870, November 24, 1987.

evaporated. Dunova, a dry-spun fiber produced by Bayer is in the first category. The fiber has an interior consisting of thousands of pores and channels, which have the ability to store water,[5] and the interior is connected to the surface by fine capillaries. The surface layer is typically 1 to 2 μm thick.[6] The configuration of this fiber allows the capillary effect to draw perspiration away from the body and then release it by evaporation.

This fiber is produced by adding a non-solvent with a low volatility, such as glycerin, to a DMF solution of acrylic copolymer; this polymer is similar to that used in standard Dralon production except for additional sulfonate dye-sites, which adds to the deep shades of dyeing even though light scattering pores are present. The non-solvent remains in the filament through the dry-spinning process and is removed during fiber washing, leaving behind a void in the fiber, which explains this fiber's ability to have a capillary effect on moisture. Hence, it is imperative one must not collapse the void during processing. The specific gravity of Dunova is 1.67 g/cm^3, which is in the normal range for an acrylic fiber.[2] This measurement indicated that the liquid had penetrated the voids. When mercury was employed for the density measurement, it resulted in a specific gravity of 0.90 g/cm^3. This measurement also established a pore volume of 23%. A water-holding capacity of 30-40 % without swelling has also been recognized.[5]

One disadvantage of acrylic fibers is their tendency toward "pilling." This is an undesirable trait for acrylic fibers because it results in the formation of unsightly balls of fiber at the fabric surface. The term to denote carpet wear is "fuzzing." This is associated with disentanglements of short staple length or breakage of longer filaments, which is followed by binding of the loose fiber to the fabric surface by other unbroken filaments. Pilling occurs to some extent with all staple derived fabrics and is affected by fabric construction, yarn

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[5] Wilschinsky, H., *Pakistan Textile J.,* 80; 1990.
[6] Korner, W., *Chemiefasern/ Textilind,* 29/81, E62 1979.

construction, fiber denier, and staple length, in addition to intrinsic fiber physical properties. A main goal of fiber producers is to reduce these undesirable characteristics, such as pilling.

One of the uses of acrylic fibers is in the production of sweaters and jersey knits where pilling is an immense problem. Some of the critics of acrylic fibers view this problem with acrylic fibers as a reason to abort them all together. The best way to combat pilling is for the fibers to release the pilled fibers from the surface before they are noticed.

The best pilling resistance was with fibers that had corrugated surfaces. This is probably due to association of the surface and structural defects that contribute to easy pill break off, which is favorable. Pilling performance is inversely related to fiber tenacity, loop tenacity, elongation, flex life, and yarn strength. Yarns with desirable pill performance were seen during processing. This was attributed to an increase in “fly” during yarn processing.

The demand for acrylic fiber is partly attributable to its low price relative to alternative fibers. There are several properties that differentiate acrylic fibers: (1) low specific gravity of 1.18 g/cm^3 (cotton is 1.58 g/cm^3), which gives bulk and value at a reduced weight; (2) soft and wool-like aesthetics; (3) brightness and ease of dyeing; (4) resistance to ultraviolet fading; (5) moisture-wicking ability and quick drying; (6) retention of shape after repeated washing. These properties make acrylic fibers good candidates for garments like sweaters, socks, fleece ware, hand knitting yarns, blankets, upholstery etc.

Acrylic fibers still play a role in today’s global economy. A significant percentage of acrylic fibers produced worldwide are exported from producing nations for final sale to consumers in importing nations. Therefore there is a need to restructure production methods for acrylic fibers. Some acrylic producers are trying to lower cost by merging with other companies. Acrylic fiber is in competition with other fibers that are worthy adversaries. Although acrylic fiber has reached a mature stage of production in the developed world, it is still growing in developing nations. These fibers are sensitive to the economy and tend to be cyclical; therefore, a recession can have a profound effect on the production of acrylic fibers, since the developed world consumes half of all the fibers that are produced. The demand for cotton and polyester fabrics have contributed to the decline in the need for acrylic fibers in the woven fabric market because acrylic fibers are not the desired fiber for this market.

As the market changed, the production and the demand did as well. Polyester fibers have introduced new competition and challenged the widespread use of acrylic fibers. One of the main reasons that acrylic fiber production was down was the development of sports companies like Russell and Champion, which required polyester/cotton blends. One reason that polyester/cotton blends were the selected choice was because of its thermal stability. The market share for acrylic fibers went from 125 million pounds in 1980 to 95 million pounds in 1991.

The high pile market demand was on the decline as well. The shift occurred when companies like BASF and Monsanto phased out acrylic fiber production. Monsanto eventually reintroduced acrylic fiber as Acrilan, which could be molded into several styles and could resist matting. Acrylian had better dyeability and durability because of the nylon/acrylic blend in a ratio of 88/12.

The onset of the energy crisis caused a revisiting of acrylic fibers for use in blankets. The lower thermostat settings offset the lower demand for acrylic fibers due to the higher energy cost. As consumers focused on conservation, the acrylic blanket lost market share because of alternatives like cotton blankets, comforters and afghans. The upholstery and home furnishings market embraced acrylic fiber once again; however, this was short lived because of the availability of substitutes and the lack of supporting programs by the fiber producers.

Acrylic and modacrylic fibers have some industrial luster since their applications include felts, battery separators, wipe cloths, sand bags, awnings, boat covers, etc. Some of these businesses have continued to grow and others have gone with the wind. The sand bag business flourished during the Vietnam War but disappeared when the war ended. In today's world, acrylic fiber will once again be required for a variety of applications due to severe weather, natural disasters, and wars. The main point that supports the use of acrylic bags is that they do not deteriorate in sunlight and jungle conditions.

Although acrylic fibers have been on the decline in developed countries, the demand is still there for some of the developing countries. It is important to recognize that there is a difference between mill demand and final demand. In most of the developing countries, mill consumption is far greater than final consumption by the local consumers. Mill consumption in these developing nations is significantly determined by the production of garments for export. Before in the 1980s, the U.S. imported more than half of its acrylic sweaters from developing countries such as Tiawan, Hong Kong, and South Korea.

Eastern Europe is another region that is expected to infiltrate the acrylic fiber game. It is estimated that this region of Europe will produce 600 million pounds per year of the acrylic fiber capacity. If political stability is achieved in a developing country, economic growth would follow, which would allow consumers to have an income to purchase more sweaters and other items that are derived from acrylic fiber.

The world of acrylic fiber is vast, yet small. This seems to be an ambiguous statement but it is not hard to recognize that the United States is a consumer nation and the rest of the world could be classified as a supplier for the United States. The United States does produce fibers and export them but not to the degree that some of our neighbors to the west and east do. The impact of some of the U. S. decisions on trade has been to allow a large influx of imported textiles - mainly acrylic fiber. The government has introduced trade policies to enhance the equality of trade among nations. Tariffs, quotas and other regulations can influence the movement of products made from acrylic fiber. It has also been necessary to change some of these laws. In 1993, Uruguay signed an agreement to lower trade barriers, which allowed for market access between developing and developed countries. Other trade agreements followed, with the General Agreement on Trade and Tariffs (GATT), which was shadowed by the North American Free Trade Agreement (NAFTA) and Europe92 played a hefty role in how acrylic fibers move through out the trade community. The NAFTA agreement encountered much protest in the United States, but it did pass.

In the early days of acrylic fiber, production was driven by substitution demand in the economically developed nations. Now that the industry has slowed due to its maturity, in some cases it has come to a grinding halt. It has been predicted that in the future, rapid growth in developing nations will result in economic development, followed by an increase in income and a boost in fiber demand once again. The growth will most likely occur in regions like Asia, China, and Latin America.

The world acrylic fiber industry is comprised of 55 producers who operate 64 production facilities in 29 countries.[2] The trend during the 1990s was that most of the unprofitable operations were shut down. Most of the facilities that were shut down were in Europe and the United States. However, Japan was able to weather the storm and keep operations going due to their well-oiled exporting business.

The acrylic fiber industry has been downsizing its operations in Europe and the United States since the early 1980s. The reason for this was the decline in demand and a resulting drop in profits. As times got more difficult, companies began to sell their production to other companies. Companies who sold or shut down their businesses included Monsanto, DuPont, and Eastman Chemical, just to name a few. Mann Industries purchased BASF in a leverage buyout in 1989. With this purchase they acquired considerable debt and had to ask their workers to take a 15% pay cut. Mann Industries suffered financially and eventually halted production of acrylic fibers in 1993.

Even Japan felt the pinch and Toray Industries ceased exports of acrylic fiber in 1998, which represented 17% of their sales or 13 million pounds per year. Several plants in Western Europe closed as well. The plants that shut down impacted countries like Italy, France, and Germany. However, a merger between acrylic and viscose fiber operations of Hoechst AG of Germany and Courtaulds PlC of the United Kingdom satisfied both companies' needs for survival. The joint venture made the two companies the second largest producers of fiber in Europe. Even though mergers, acquisitions, and company shutdowns have plagued the industry, the expected growth is still in the developing countries. In 2002, 6.3 billion pounds of acrylic fiber were produced, which is 1 billion pounds greater than the 1990s, and 75% of that growth was in the Far East.[2]

Nylon variants, polyester, and olefin are used to produce carpets that easily can be rinsed clean, even 24 hours after staining. Stretchable spandex and machine-washable, silk-like polyesters occupy solid places in the U.S. apparel market.

There are certain applications needed for the polymerization of acrylonitrile to become fibers. The route best suited for this is free radical polymerization because it gives better control of rate and other properties, such as whiteness, molecular weight, linearity, and the ability to incorporate comonomers and dye sites.

Acrylic polymers for textile application usually have a number average molecular weight in the range of 40,000 to 70,000 g/mol. The weight average molecular weight is typically around 90,000 to 170,000 g/mol, with a polydispersity index between 1.5 and 3.0. Higher molecular weight polymers are necessary for applications where more strength is required, such as cement reinforcement and carbon fiber precursors. In cases such as these, the molecular weights could be as high as 250,000 g/mol.

The solubility of a polymer and the rheological properties of a dissolved polymer must be precisely defined for dry or wet spinning. The polymer molecular weight is affected by such variables as initiator concentration, unreacted monomer concentrations, comonomer type and concentration, reaction temperature and time. The dyeability of fiber is dependent on molecular weight distribution. The reason for this is that acrylic fibers derive their dyeability from sulfonate and sulfate initiator fragments at the polymer chain ends. Thus, the dye site content of the fiber is inversely related to the number average molecular weight of the polymer and is especially sensitive to low polymer molecular weights.

It is important that the polymer is linear so that it may be spun over a wide range of molecular weights at the necessary concentrations, while considering the solvent and spinning conditions. The most economical way to keep cost low is to spin fiber from the highest concentration of spin dope; this means that there is less solvent to recover per unit fiber produced.

There are several polymerization methods by which reactions may be carried out. For example, bulk polymerization is the most fundamental of the methods to be mentioned but its commercial use is limited by its autocatalytic nature. Aqueous dispersion polymerization is a variant of suspension polymerization, which is the most common commercial method. Solution polymerization is used in cases where the spinning dopes can be prepared directly from the polymerization reaction product. Emulsion polymerization is mostly used with modacrylic compositions where a high level of a water-insoluble monomer is used or where the monomer mixture is relatively slow reacting. The method of polymerization chosen for this research was emulsion polymerization. Although emulsion polymerization and free radical processes go hand in hand, this method has all but vanished as a method to produce acrylonitrile polymers for fiber end use. Emulsion polymerization has an advantage of segregating radicals from one another by trapping them in monomer micelles. Normally only one radical infiltrates a micelle and recombination is not possible unless a second radical diffuses into the same micelle - thus higher molecular weights and rates of polymerization may be achieved. Emulsion polymerization was quite popular with companies like Monsanto, Union Carbide, and Cytec for the production of their fibers.

Emulsion polymerization is a very complex topic; so, this brief overview will discuss only the basics of the technique. In emulsion polymerization, a small amount of monomer is added to the reaction vessel and the emulsifier (surfactant or soap) disperses the monomer into aggregates of 50-100 molecules with a micelle diameter of 50 Å. The remaining monomer is in droplet form (10,000 Å diameter) and is the reservoir that replenishes the micelles. Water-soluble initiators such as ammonium persulfate, potassium persulfate, and sodium bisulfite are responsible for initiation of polymerization. The radicals formed in the aqueous phase are rapidly captured by the micelles.[7] Polymerization occurs rather quickly within the micelles with additional monomer being supplied by the droplets. The number of micelles remains constant relative to the amount of surfactant. The ideal situation is when a radical enters a micelle and initiates polymerization in that micelle and is terminated via recombination when another radical

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[7] R.M. Fitch , Lih-bin Shih,*Prog. Col. Polym. Sci.,* 56; 1 1975.

enters that micelle. It resumes when a third radical enters, etc. Monomers like acrylonitrile can deviate from ideality because the growing chains can desorb from the micelle.[2] Conditions that favor desorption are small particle size, high acrylonitrile (AN) water solubility, elevated chain transfer activity, especially with a water soluble agent and low particle swelling by AN monomer. Under such conditions, the radical population may be extremely low.[2] These are a few factors that may enhance or retard the efficiency of emulsion polymerization, although there are many more. The main examples of emulsion polymerization of acrylonitrile for fiber end use have been for modacrylic flame-retardant fibers based on vinyl chloride. The emulsion polymerization process isolates the radicals from each other and other potential transfer agents in aqueous phase and thus allows production of polymer with adequate molecular weight for fiber applications. This explanation of emulsion polymerization is not meant to oversimplify a very complex reaction that can affect how fiber properties may be influenced via the emulsion polymerization variables.

The industrial uses for manufactured fibers are very diverse and include super absorbent diapers, artificial organs, and construction materials. This industry has grown by leaps and bounds. There is no question that fibers have influenced the scientific community immensely.

Carbon Fiber Precursors

Acrylic fiber is a major precursor for carbon fiber production, although rayon and pitch are also used. In some respects, carbon fiber precursors require the same properties that are needed for reinforcing fibers. However, the most important factor for the production of carbon fiber is the ease of stabilization of product. The stabilization is achieved by the formation of a ladder polymer through dehydrogenation or nitrile polymerization (Fig. 1).

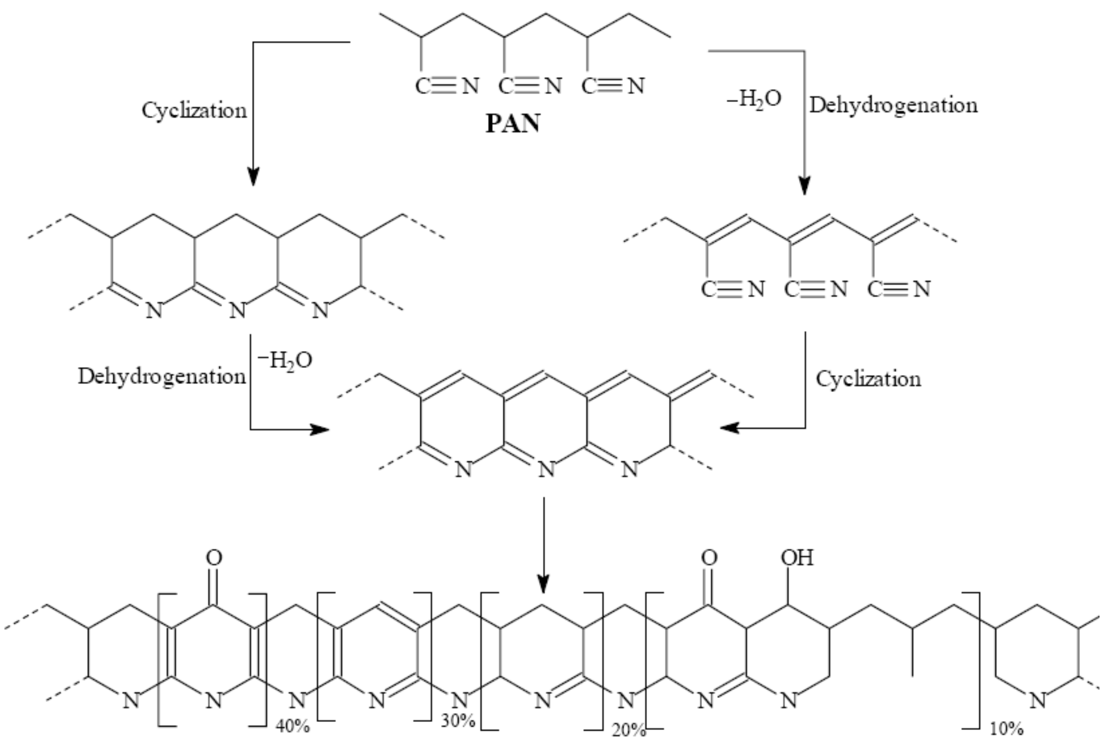

Figure 1: Proposed Chemistry of PAN stabilization[8]

During the stabilization process, volatiles are observed, which are H_2O, CO_2, and HCN. However, about 8-10% oxygen still remains in the "stabilized" polymer in the form of ketones and hydroxyl groups. These reactive groups might very well contribute to further intermolecular crosslinking. If a stabilized fiber contains more than 12% oxygen it usually denotes that the fiber is mechanically not sound and a fiber with less than 8% is low in carbon content, which correlates with high weight loss during the carbonization step.[6]

Oxidation stabilization causes shrinkage, which is about a third of the overall dimension of the fiber. The shrinkage is due to the chemical cyclization crosslinking and the dehydrogenation reaction and by molecular relaxation.[9] At 200 °C relaxation and shrinkage is complete; however, chemical shrinkage becomes increasingly important. The shrinkage due to

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[8] Bansal, R. C.; Donnet, J. B. *Carbon Fibers 2nd Ed.*; Marcel Dekker Inc.: New York, 1994.
[9] Fitzer, E.; Frohs, W.; Heine, M. *Carbon* **1986,** *24*, 387.

relaxation above T_g can be controlled by restraining the fiber under constant force or in a longitudinal direction during the “stabilization” step.

The next step in the evolution of PAN fibers is thermal pyrolysis in an inert environment where the non-carbon elements are removed as volatiles. This process produces about 50% carbon yield of carbon fiber when PAN homopolymer is used. The initial process of thermal pyrolysis occurs at 300-600° C and involves chemical reactions which produce HCN, CO_2, NH_3, and H_2O as volatiles and hydrocarbons in the form of tar. The degree of stabilization of the PAN fiber correlates with the amount of tar that is produced. The velocity of volatile evolution is dependent on the heating speed, which is usually kept low (about 1.5 °C/min). The fibers can be damaged if they are heated too fast; this results in fibers with low carbon content. During the first stage, it has been proposed that the oxygen-containing groups initiate the crosslinking condensation reaction. That produces a fixed structure, while other linear segments become cyclised or undergo chain scission. The next stage of thermal pyrolysis is preformed at 600-1300 °C and consists of cyclised structures undergoing dehydrogenation as well as linking in the lateral direction. These heterocyclic molecules become oriented and become graphite-like and evolve nitrogen and hydrogen. Carbonizing in an atmosphere of hydrochloric acid vapors may increase carbon yield by as much as 50%. The third and final stage of pyrolysis is carried out at 1300-2500 °C, which is the graphitization temperature. The improved orientation of the crystallites in the direction of the fiber axis, without any noticeable weight loss, is achieved by the heat treatment (a few seconds). This process produces a superior product with excellent mechanical properties; which results in a high-performance carbon fiber suitable for many applications.[10]

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[10] Edie, D. *Carbon* **1998,** *36*, 345-362.

Carbon fibers are appealing for many applications because they are lightweight and have excellent strength, stiffness, chemical inertness, thermal and electrical compatibility, and vibrational characteristics, The problem if any is that at low extension the fibers fracture and do not have good impact resistance. The high cost of carbon fibers limits them mostly to expensive technology applications. The recent focus has been on finding ways to lower cost and to increase the number of applications, especially for the auto industry.

Aerospace and nuclear engineering are two modern applications of carbon fibers. Another application is in the general transportation and engineering domain. This involves fibers being used for such things as camshafts, fan blades, bearings, and automobile bodies. These lightweight materials can enhance fuel mileage for aerospace as components on aircraft. For the general uses the carbon fibers must have more than one benefit such as low cost and still maintain their mechanical properties; this is a difficult order to fill. Acceptable matrices, material forms and manufacturing methods need to be found in order to recognize the differences in the two areas of carbon fiber use.

Unidirectional anisotropic reinforcement is a characteristic of carbon fiber materials. This means that the fibers can be arranged in such a way that the material produced is much stronger in one direction, where its obligation is to bear loads. The complexity that is needed requires the fiber to resist deflection while maintaining high performance in more than one direction. Hence, operation under different mechanical, physical and chemical environments is required in these applications. In order to fit these requirements, it is necessary for the fiber to be arranged in layers in more than one direction to increase the effectiveness. Designers are able to selectively change these layered arrays to fit the custom needs of reinforced carbon fibers. The use of reinforcement material for certain applications is being realized, but there is no one fiber that can satisfy all technical and economical requirements. Hence, development of a variety of reinforcement fibers that have different mechanical, electrical, and physical properties is leading the way in carbon fiber technology. Kevlar can be used as a secondary reinforcement material combined with carbon fibers to produce a composite material with increased impact strength than carbon fiber single-handedly and better compressive strength than Kevlar alone. The hybrid fibers may consist of glass fibers, boron fibers, Kevlar fibers and carbon fibers, etc. The differences in hybridization within the matrix can consist of using two or more fibers in the same fabric, called intraply hybrid, or the fiber plies can be mixed through the composite cross section, called interply hybrid.[6] Table 1 indicates some applications of carbon fiber composites on the basis of their most significant mechanical and physical properties.

Table 1: Application of carbon fiber composites on the basis of their most significant mechanical and physical properties[6]

Physical strength, specific toughness, light weight	Aerospace, road and marine transport, sporting goods
High dimensional stability, low coefficient of thermal expansion, and low abrasion	Missiles, aircraft brakes, aerospace antenna and support structures, large telescopes, optical benches, waveguides for high-frequency (GHz) precision measurement frames
Good vibration damping, strength and toughness	Audio equipment, loudspeakers for Hi-Fi equipment, pickup arms, robot arms
Electrical conductivity	Automobile hoods, novel tooling, casings and bases for electronic equipments, EMI and RF shielding, brushes
Biological inertness and X-ray permeability	Medical application in prostheses, surgery and X-ray equipment, implants, tendon/ligament repair
Fatigue resistance, self-lubrication, high damping	Textile machinery, general engineering
Chemical inertness, high corrosion resistance	Chemical industry; nuclear field; valves, seals and pump components in process plants
Electromagnetic properties	Large generator retaining rings, radiological equipment

A desirable property of carbon fiber is the specific strength, stiffness and light weight. Compared to steel, carbon fiber composites have much greater mechanical properties and are lighter in weight by 45-75%. The other physical properties of carbon fiber, like thermal conductivity and corrosion resistance can be optimized by changing the matrix material and the processing conditions for the production of carbon fibers or reinforced polymer matrix composites (PMC).

Acrylonitrile Copolymers and Fibers

Today one of the leading countries for the advancement of modified fibers is Japan.[11] Some of the most desirable characteristics are fibers that have such properties as high persistence, reduced elongation, permanent softness, lustre, micro pores, acid dyability, water resistance, and flame resistance. These are just some of the available uses for acrylic fibers today. As well as being desirable, these new fibers are functional because of their ability perform in several different arenas such as civil engineering, composite materials, asbestos replacement, hollow ion exchange fibers, and precursors for high strength carbon fibers.

Textile grade acrylic fibers have less stringent production requirements than high performance acrylic fibers, although precautions must still be taken to produce a first-class fiber. The physical and chemical properties of these structures are sensitive to chemical composition, molecular weight, molecular weight distribution, spinning and post spinning parameters. For an acrylic fiber to be classified as such it must have 85% acrylonitrile monomer incorporated into the copolymer to meet the criteria.

The use of comonomers with acrylonitrile can produce a variety of specialty fibers that may be used for different applications. A few of the comonomers used in carbon fiber precursors

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[11] Sen, K.; Baharami, S. H.; Bajaj, P. In *High Performance Acrylic Fibers, in J. M. S. Revue of Macromolecular Chemistry Phys.*; Marcel Dekker Inc.: New York, 1996; Vol. C36; pp. 1-76.

are shown in Table 2. The homopolymer of acrylonitrile PAN has inferior properties in carbon fibers, compared to PAN copolymers. Enhanced mobility of polymer segments or a decrease in the glass transition temperature (T_g), usually occurs when a small percentage of a comonomer is added. The addition of the comonomer depresses the onset of cyclization temperature for the period of oxidation and improves the spinability. Consequently, this decreases the crystallinity and the crystallite size.

Manufacturing of acrylic fibers requires a copolymer with some dye sites, specific molecular weight and controlled composition. Therefore, the copolymerization process is an extremely important step in the manufacturing of acrylic fibers.

Methyl acrylate (MA), methyl methacrylate (MMA) and vinyl acetate (VA) are the regularly used comonomers (Fig. 2). They increase the solubility and change the morphology of the fiber. Comonomers also improve the rate of diffusion of the dye into the fiber. The amount of neutral comonomers in commercial fibers is typically 2-15 mole percent or 5-20 weight percent. When dry spinning is the method of fiber production, MA is used as the comonomer over VA because VA reduces the stability of the spinning dope at increased temperatures in the spinning tower.[12,13,14]

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[12] Bajaj, P.; Padmanabhan, M. *Eur. Polym. J.* **1984,** *20*.

[13] Bajaj, P. In *Manufactured Fibre Technology;* Gupta, V. B.; Kathari, V. K. Eds.; Chapman and Hall: London, 1997; pp. 407-454.

[14] Bajaj, P. *Polymer* **2001,** *42*, 1707-1718.

Table 2: Table of comonomers commonly incorporated into acrylic precursors.[15]

Various Comonomers for Acrylic Precursors	
Comonomer	Chemical Structure
Acrylic acid (AA)	$CH_2=CHCOOH$
Methacrylic acid (MAA)	$CH_2=C(CH_3)COOH$
Itaconic acid (IA)	$CH_2=C(COOH)CH_2COOH$
Methylacrylate (MA)	$CH_2=CHCOOCH_3$
Acrylamide (AM)	$CH_2=CHCONH_2$
Aminoethyl-2-methyl propenoate(Quaternary ammonia salt)	$CH_2=CH(CH_3)COOC_2H_4NH_2$

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[15] Gupta, A. K.; Paliwal, D. K.; Bajaj, P. *Journal of Macromolecular Science-Reviews in Macromolecular Chemistry and Physics* **1991**, *C31*, 1-89.

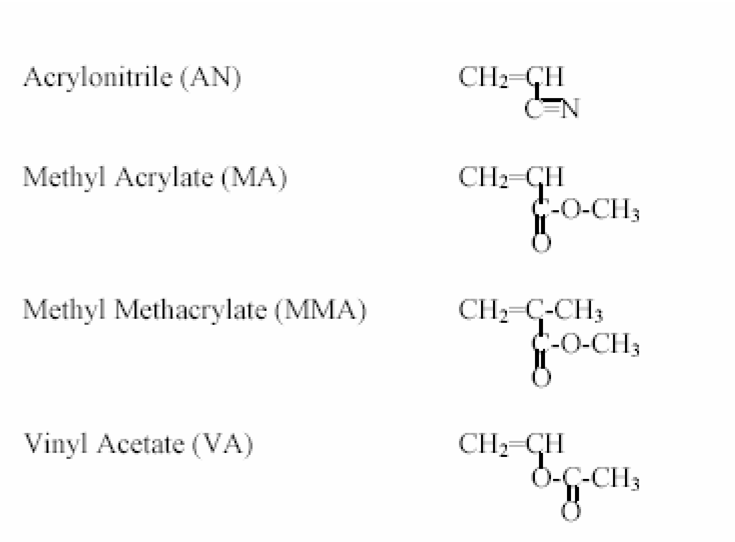

Figure 2: Chemical structures of common comonomers in acrylic fibers.

Sodium-*p*-styrene sulfonate, sodium methallyl sulfonate and sodium 2-methyl-2-acrylamido-propane sulfonate are examples of ionic comonomers which can be used in the copolymerization process. They all provide dye sites and improve water sorption. Around 30-50 meq kg^{-1} of sulfonate and sulfate dye sites are needed for acrylic fibers colored with cationic dyes.[16]

Several methods for polymerization have been successfully used to make homo- and copolymers of acrylonitrile, including solution, suspension and emulsion polymerizations.[11] Solution polymerization is the most widely used technique to produce acrylic polymer fibers. Both homo and copolymers of acrylonitrile use this method because it has the advantage that one can spin the polymer directly after the polymerization process. The unreacted monomers must, of course, be removed and the spinning dope viscosity needs to be controlled. Usually, a homogeneous medium is used for the reaction and solvents such as N,N-dimethylformamide (DMF), N,N-dimethylacetamide (DMAc) and dimethylsulfoxide (DMSO), are generally used.

To initiate the reaction, thermally activated free radical initiators like azobisisobutyronitrile (AIBN) and redox systems like ammonium persulfate and sodium persulfate can be employed. Anionic and free radical initiators are the only options to accomplish initiation of polymerization of acrylonitrile. Anionic polymerization involves nucleophilic addition to the vinyl group, but it may also attack the nitrile group, which is not desirable.

Although solution polymerization is advantageous as discussed above, there are limitations. Comonomers such as vinyl acetate and vinyl chloride are not easily used because of unfavorable reactivity ratios and inferior color in the resulting polymer. In order to dry-spin the polymer, a solvent that has a relatively high boiling point must be

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[16] Bajaj, P. In *Manufactured Fibre Technology;* Gupta, V. B.; Kathari, V. K. Eds.; Chapman and Hall: London, 1997; pp. 407-454.

used and the choice is usually DMF.[17]

Suspension polymerization is another very important technique used to produce acrylic fibers. Aqueous suspension polymerization uses water as a convenient medium for heat transfer and the polymer is very easy to recover by simple filtration. Solvent-water suspension polymerization is a technique where water is used with solvent in about equal proportions by weight at the beginning of the reaction. Later during polymerization, more water is added to reduce chain transfer to solvent.

Inorganic radical generators, like persulfates, and organic initiators, like AIBN, are used in suspension polymerization.[18] Ammonium or potassium persulfates as oxidizers and sodium bisulfite as a reducing agent are the most common redox systems used. The kinetics are similar for solution and suspension polymerizations, but termination is usually by radical recombination in suspension systems. The chemical and physical properties of the polymer, such as molecular weight and concentration of dye sites, vary according to solvent/monomer ratio, bisulfite/persulfate ratio, reaction temperature, pH of reaction slurry, addition of chain stopping agents, and agitator speed.

Wet and dry spinning are the techniques that are most often used for the production of acrylic fibers. Melt spinning is not yet possible because the acrylic precursor will degrade before it reaches its melting point. It is rare that homopolymers are used for fiber spinning and nearly all commercial acrylic fibers are spun from acrylonitrile polymers containing about 5-10% comonomer. The comonomers are added a few reasons. A polymer spun from PAN homopolymer is very difficult to dye because the large dye molecules have difficulty in penetrating. This problem is alleviated by the addition of comonomers such as methyl acrylate or

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[17] O'Donnell, J. P.; Haddleton, D. M.; Morsley, D. R.; Richards, S. N. *J. Polym. Sci.* **1999,** *37*, 3549-3557.
[18] Kim, B. K.; Oh, Y. S.; Lee, Y. M.; Yoon, L. K.; Lee, S. *Polymer* **2000,** *41*, 385-390.

vinyl acetate, which disrupt the laterally bonded structure and allows for rapid diffusion of the dye molecules during the dyeing process. There are additional benefits as well. For instance, the copolymers are more soluble than the PAN homopolymer, which makes preparation and storage of the spinning dopes easier, and the resulting fiber is more extensible and less prone to fibrillation, although the hot-wet strength and modulus is reduced relative to fiber spun from the homopolymer. The incorporation of a comonomer generally reduces the crystalline network and lowers the melting point in a continuous mode. This occurs because the new comonomer is only rarely isomorphous, i.e., will fit into the crystalline lattice of the homopolymer.[2] In the following discussion of acrylic fibers, the major comonomer will be acrylonitrile and the other comonomers like vinyl acetate (VA) or methyl acrylate (MA) will be the minor components.

In the classical model developed by Flory, the assumption was that copolymer crystallizes in a manner that places the minor component in the amorphous domain.[19, 20] The crystalline phase is formed by the parallel arrangement of uninterrupted sequences of the major comonomer (in this case, AN) and alignment of chain segments. However, the presence of the minor component (MA or VA) reduces the average length of the AN segments. This reduces the number and average size of the crystallites. By reducing the size of the crystallites, this increases the surface-to-volume ratio of the crystallites. The chain segments on the surface of the crystallites have a larger free energy than those away from the surface. When the surface-to-volume ratio is increased, the free energy of the crystal increases as well; this causes the melting point to be lowered.

Flory derived an equation to explain how the minor comonomer (MA or VA) could affect the crystalline homopolymer's melting point (Figure 3).

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[19] Flory. P.J., *Trans Farady Soc.,* 51; 848 1955.
[20] Wunderlich, B., *Macromolecular Physics, vol. 3,* Acdemic Press, New York, 1980. p.275.

$$\frac{1}{Tm} - \frac{1}{Tm^{\circ}} = \frac{R}{\Delta H_{\mu}} X_{B}$$

Figure 3: The melting point equation derived by Flory[21]

In this equation, T_m and T_m^0 are the melting points of the copolymer and the homopolymer respectively, R is the gas constant, ΔH_μ is the heat of fusion per mole of crystalline repeat units, and X_B is the mole fraction of the minor comonomer. This equation attempts to explain how these minor comonomers may affect the melting point, which is critical in processing. The role of the comonomer is statistical, and that is to restrict the sequence length of the major crystalline comonomer.

An alternate theory to Flory's is the proposed "defect crystal" model by Eby.[22] This theory states that the defects in the crystal lattice disrupted the intermolecular interactions, which is responsible for the decrease in the melting point. Even though this theory is thought to be different from Flory's it is functionally similar to the previous theory. This "defect crystal" model also predicts a linear relationship between the reciprocal melting point and the mole fraction of the comonomer. However, another parameter is valid in evaluating how a comonomer disrupts the crystal lattice. With this model, a particular comonomer depresses the melting point to a first approximation proportional to the molar volume of the comonomer. The slope of the reciprocal melting point versus comonomer mole fraction curve is no longer inversely proportional to the heat of fusion of the homopolymer, as with Flory's theory. The slope can be interpreted as an approximation of the degree to which the comonomer disrupts the lattice.

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[21] Flory, P. Principles of Polymer Chemistry, Cornell University Press: Ithaca, NY, 1953.

[22] Eby, R. K., *J. Appl. Phys,* 34; 2442, 1963.

Melt processing can be accomplished by adding comonomers that decrease or eliminate the melting point (T_m). The T_m may also be depressed by the use of plasticizers, solvents and the addition of water under pressure. It has been reported that under pressure the water can hydrate the nitrile groups, which allows the melt to be extruded.[15] The wet spinning process uses a spinning dope that is extruded through a multihole spinneret into a non-solvent coagulation bath. After the dope jets coagulate into solid filaments and are then removed from the spinning bath, they are washed in hot water to remove the rest of the solvent. The fiber is drawn and subjected to drying, crimping and annealing. The linear speed of fiber formation by solution spinning is extremely slow in comparison to melt spinning. Therefore, to obtain an economically feasible fiber, many spinnerets having multiple thousands of holes are used. Then, the filaments from many spinnerets are combined to make the required denier. The dope preparation is done in a variety of solvents and the polymer concentration is dependent upon which solvent is used. Usually the concentration ranges from 10-25% solids. Solution polymerization dope uses the same solvent as the polymerization process. Aqueous slurry (suspension) polymerization recovers the polymer by filtration to form a wet polymer cake. Therefore, the spinning dope solution is an aqueous salt solution where the polymer cake can be dissolved directly.[23] By degassing the filtered dope, which contains 10-25 weight percent polymer, fiber extrusion is performed by spinning it through spinnerets with 10,000-60,000 holes, which can range from 0.05 to 0.38 mm in diameter. The fiber is then strung into a liquid bath that contains a non-solvent for the polymer. After the solvent is removed, fiber formation happens rapidly during the coagulation of the polymer material.

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[23] Ebdon, J. R.; Huckerby, T. N.; Hunter, T. C. *Polymer* **1994,** *35*, 250-256.

Dry spinning is the other common technique used to produce acrylic fibers for industrial goods. The dope solution contains a higher amount of polymer, 30-32% by weight. Furthermore, the rate of dry spinning is much faster than the rate of wet spinning, e.g. 200-400 meters per minute and 3-10 meters per minute respectively. The extrusion process uses a spinneret with only 1500-2500 holes, which is placed at the head of a two-chamber vertical tower that is 5-6 meters high. In the tower, there is inert gas, preheated to 300-400 °C. The upper cell of the tower contains inert gas, such as nitrogen, at 350-400 °C that flows from top to bottom to remove the solvent. The solvent is recovered by distillation and the gas is then recycled after being heated again. The lower column uses a lower temperature that helps to cool the fiber bundle and also removes more solvent. The solvent is once again removed from the gas by distillation and the gas is then recycled after pre-heating. The fibers that leave the two-column tower may still contain 10-20% solvent. Compared to wet-spinning, the dry spinning process is more expensive because of the complex system requirements in the column. The gas circulation, the solvent recovery techniques, and the heating are all expensive processes. The comparison of the fibers using DMF as the solvent shows that the dry spun fibers have higher bulkiness and can recover from deformation better. The wet spun fibers are softer and fleecier and have a better dye pick-up. The wet spinning process is recommended when a low denier fiber with fine thread is needed, 1.2-3.0 denier (grams per 9000 meters).[12]

The high price of solution and suspension acrylic fibers has driven a search for more economical methods of producing fibers. The high cost mainly comes from the use and disposal of the solvent, but can also be attributed to the slower rates of processing and the expensive equipment needed for processing. Thus, the aqueous dispersion copolymerization of acrylonitriles and acrylates would be expected to decrease the cost for solvents and the environmental impact from disposal of these solvents. Furthermore, the development of melt spinnable PAN copolymers would be expected to reduce the cost by increasing the rate and ease of processing at comparable volumes.

Melt Processing

There are some basic requirements that are needed for a PAN fiber to be melt spun. There are also additions that can aid in the feasibility of acrylic fibers being melt spun. This will be discussed in greater detail later.

The melting point (T_m) of polyacrylonitrile is around 320 ºC.[24] Chemical changes start to occur well below the melting point. In order to spin polyacrylonitrile from the melt, the melting point must be reduced drastically by about 120 ºC.

There have been several attempts to reduce the melting point and/or melt viscosity of the polymer in order to develop a more economical solvent-free melt spinning process for high quality PAN fibers. The main reason for the high melting point is the low entropy of fusion (ΔS_m). This means that the melting temperature is $T_m = \Delta H_m/\Delta S_m$. The polyacrylonitrile molecule becomes helical because of the strong electrical interactions between neighboring CN dipoles. The helices are not destroyed in the melt but the intramolecular interactions are diminished. However, the increase in entropy during melting is small, which has little effect on lowering the T_m. To bring the melting point of the polyacrylonitrile below 200 ºC, the intramolecular interactions of the CN dipoles must be disrupted. This can be done chemically with the addition of comonomers. Addition of comonomers increases the distance between the CN pendant groups and disrupts the sequences of CN.

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[24] Hinrichsen, G., *Macromol, Chem.,* 20, 121, 1971.

Another way of weakening the interactions between the CN dipoles is by surrounding the CN groups with other dipoles. Some of the molecules for this task would be water, which forms hydrogen bridges to the nitrogen atoms. Water is very mobile and it takes up little space and diffuses through the melt easily and rapidly. One must keep in mind that water is in demand and must be conserved. Although it is a good option for the task there are others also, including glycols and glycerin. These compounds form hydrogen bridges with the nitrile groups via their hydroxyl moieties. The reduction in the dipole interaction depends on the dipole moment. One attractive feature of the use of water and glycols is the fact that they can easily be removed form the fibers afterward.

Acrylic esters or methacrylic esters can be used as the comonomers to aid in lowering the melting point. For example, a copolymer containing 85% acrylonitrile and 15% methacrylic ester results in a reduced viscosity of 0.62. If 11% of the polymer is extracted with acetone, η_{red} increases to 1. The melt can be spun at 1500 m/min at 200 °C. After hot drawing at a ratio of 4.5, a 1.8-denier fiber with a tenacity of 4.5 g/den is obtained.[25]

It has been established that as the comonomer content increases, so does the heat shrinkage of the draw down as well. This can be attributed to the weakening of the CN interactions by statistical distribution of comonomers. This could be viable on an industrial scale if the copolymer can partially crystallize to counteract the tendency to shrink. There are other alternatives that are being developed currently, including the systematic variation of polymerization variables reported herein. The end goal is a melt-processable carbon fiber precursor which is not subject to the problems currently associated with melt-processing.

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[25] Mitsubishi, Japan patent, 1,160,416,27.12 (1984)

A number of commercial polymers, including Kevlar, acrylic (PAN) fibers and Lycra, are currently produced using solution-based processes. Solution produced polymers usually require the use of toxic, organic solvents, commonly including DMF and DMAc, to process the materials into their desired final form. These solvents are extremely undesirable from an environmental standpoint. Solvents are typically used to make a material processable at a lower temperature to prevent degradation or to produce materials difficult to obtain via conventional processing techniques. In the case of PAN systems, solvents are required to prevent degradation of the material prior to fiber formation. Concern over volatile organic solvent emissions has initiated searches to find cleaner solvents for polymer synthesis and processing.[26] Certain supercritical gasses, such as supercritical carbon dioxide (Sc-CO_2), are recognized as plasticizers for certain polymer systems. The Sc-CO_2 in this system reduces the glass transition temperature, leading to a melt viscosity reduction and allowing processing to occur at lower temperatures. There are several benefits to the use of carbon dioxide over organic solvents. Carbon dioxide is non-toxic, non-flammable, environmentally friendly, completely recoverable, and easily obtained in its supercritical form (T_c=31.1 ^oC, P_c=1073 psi). The supercritical state of CO_2 is desirable because it is known to have analogous solubilization characteristics to organic solvents, such as hexane and CFCs and is well known to plasticize a number of amorphous polymers.[27, 28] Sc-CO_2 possesses a diffusivity similar to that of a gas, but a density that mimics a liquid, which promotes rapid plasticization in amorphous materials.[29] This could be the reason that Sc-CO_2 is such a

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[26] Cooper, A.; Howdle, S. *Materials World* **2000**, *8*, 10-12.

[27] Shieh, Y. T.; Su, J. H.; Manivannan, G.; Lee, P. H. C.; Sawan, S. P.; Spall, W. D. *Journal of Applied Polymer Science* **1996**, 59, 707-717.

[28] Shieh, Y. T.; Su, J. H.; Manivannan, G.; Lee, P. H. C.; Sawan, S. P.; Spall, W. D. *Journal of Applied Polymer Science* **1996**, 59, 695-705.

[29] Garg, A.; Gulari, E.; Manke, C. W. *Macromolecules* **1994**, *27*, 5643-5653.

desirable replacement for solvent-based applications. The versatility demonstrated by Sc-CO_2 has propelled it to the front of the commercial application line.[59]

Companies are becoming increasingly conscientious about maintaining the environment due to strong outside pressures. Replacing unfriendly, environmentally toxic solvents with friendly fluids is a major motivation in today's chemical industry. These solvents are used in a host of various applications, such as ceramics processing, paper deacidification, metal cleaning, and plastics and textiles processing.[30] Supercritical carbon dioxide is the "silver bullet" fluid that is commonly used in a broad variety of applications and has been a crucial point for numerous pioneering studies. Supercritical carbon dioxide use has been studied in novel polymerization techniques, microcellular foaming processes, morphology control, extraction of impurities, and even impregnation of polymers with various materials. Some of the various commercial applications for Sc-CO_2, and the stage of development, are given in Table 3.

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[30] Moore, S.; Samdani, S.; Ondrey, G.; Parkinson, G. *Chemical Engineering* **1994**, *101*, 32.

Table 3: Commercial applications of $ScCO_2$ with corresponding stages of development

Status	Application	Companies
Commercial	Spray Painting without VOCs	Union Carbide Corp. (Danbury, CT)
Commercial	Deasphalting	Kerr-McGee Corp (Oklahoma City, OK)
Developmental	Ceramics Processing	Fairey Industrial Ceramics Ltd. (Filleybrooks, U.K.)
Developmental	Paper Deacidification and Preservation	France's Energy Commission (Pierrelattie) & Separex S.A. (Champigneulles)
Developmental	Metal Parts Cleaning	Joint Assn. for Advancement of SCFs
Commercial	Metal Parts Cleaning	CF Technologies (Hyde Park, MA)
Pilot	Thermoplastics Processing	Axiomatics Corp. (Woburn, MA)
Developmental	Textile Dyeing	Batelle Pacific Laboratories (Richland, WA)
Developmental	Separation Plastics Recycling	Tohoku Univ.

Polymerization in CO_2 has proven useful for materials that are difficult to synthesize with traditional methods. Energetic polymers and pyrotechnics are typically processed with volatile organics and ozone-destroying substances. Hence, high-pressure liquid carbon dioxide is desirable because it has been shown eliminate the need for these solvents. It also acts as a precipitator for such materials as poly-3-nitratomethyl-3-methyl oxetane and magnesium, Teflon and Viton pyrotechnic material.[31] The use of this method almost completely eliminates any hazardous waste generation. Furthermore, CO_2 is easily removed following polymerization, which eliminates another step in the processing of such materials. The use of Sc-CO_2 has also proven effective in the polymerization of polyacrylonitrile (PAN), which traditionally requires the use of aqueous and/or organic solvents. Most industrially important hydrocarbon-based polymeric materials are insoluble in CO_2, but a heterogeneous polymerization in Sc-CO_2 has proven to be successful for PAN when stabilized with PS and poly(1,1- dihydroperfluorooctyl acrylate).[32] The molecular weight of the resulting acrylic polymer can be manipulated by controlling the pressure or temperature in a closed system of Sc-CO_2.

In many processing situations, it is desirable to introduce additives to a product. This is often the case with glassy polymers because the diffusion into these materials is dreadfully slow. When exposed to Sc-CO_2, and even high pressure CO_2 gas, a number of glassy polymeric materials are plasticized into the rubbery state, which improves and accelerates impregnation with additives.[33] The CO_2 swells the glassy polymeric materials, which allows controlled diffusivity. The phase separation conditions may be regulated as well, which in turn regulate impregnation. The polymers that are known to undergo plasticization rapidly and impregnation

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[31] Farncomb, R. E.; Nauflett, G. W. *Waste Management* **1997**, *17*, 123-127.

[32] Shiho, H.; DeSimone, J. M. *Macromolecules* **2000**, *33*, 1565-1569.

[33] Berens, A. R.; Huvard, G. S.; Korsmeyer, R. W.; Kunig, F. W. *Journal of Applied Polymer Science* **1992**, *46*, 231-242.

in the presence CO_2 include poly(vinyl chloride), polycarbonate, poly(methyl methacrylate), and others. The plasticizing behavior of Sc-CO_2 can also be very useful for decreasing the melt viscosity in amorphous polymer melts. Controlling viscosity to regulate the rheological properties of polymer melts or solutions at the final processing stage has sparked considerable interest. One example is the extrusion of cornstarch using CO_2 as a blowing agent.[34] The addition of Sc-CO_2 has also been found to plasticize, swell, and reduce the melt viscosities of several polymeric materials, one of which is poly(methyl methacrylate), although there are several others.[35] Reduction of melt viscosity permits processing at lower temperatures, which can be of great importance when working with thermally unstable materials such as PAN.

Although limited studies have been performed in continuous high-pressure extrusion to study microcellular foams and polymer blending using CO_2, the improvement in processability of polymer systems due to suppressed melt viscosities has not been fully understood or explored. In order to effectively incorporate Sc-CO_2 into a process, it is important to understand the characterization of a plasticized system, thermodynamically as well as chemically. This will assist in facilitating an understanding of the rheological effects of plasticization.

Carbon fiber precursors yesterday and today are acrylic based textile fibers currently produced using environmentally unfriendly wet or dry fiber spinning processes. Solvents are difficult to dispose of, but they must be utilized in the solution spinning processes, which adds to the high cost of producing carbon fibers.[36] Additionally, the solution spinning process requires the removal of solvent from the precursor. This could lead to a weight loss of as much as 80%, which lends itself to a low carbon yield. A competing cyclization reaction that degrades the resin

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[34] Lee, F. Y.; Ryu, G. H.; Lim, S. T. *Cereal Chemistry* **1999**, *76*, 63-69.

[35] Royer, J. R.; DeSimone, J. M.; Khan, S. A. *Journal of Polymer Science Part B-Polymer Physics* **2001**, *39*, 3055-3066.

[36] Bortner, M. J. Ph.D. Thesis,Virginia Polytechnic Institute and State University. VA, 2003.

at melt processing temperatures also creates a problem and limits the processing window for these materials. The focus of this research is to develop and establish the processing window for an acrylonitrile-based resin that can be melting spun into fiber. By doing this, the need for solvent recovery can be eliminated. This would result in a higher carbon yield, lowering the cost per pound of carbon or textile fibers. Conventionally, PAN copolymers are solution spun into textile fibers and carbon fiber precursors. The comonomer used with the acrylonitrile, usually MA, lowers the viscosity of the resin and hinders the degradation that occurs at processing temperatures. The solution-spun copolymer typically has a melt viscosity much too high for a melt spinning process, which when combined with the thermal degradation requires a solution spinning process. For a melt spinning process, the melt viscosity of the starting resin would have to be much lower than that used in current commercial processes, requiring higher comonomer content. The dichotomy of this situation leads to one of several problems in resolving this phenomenon.

The introduction of various chemical structures and composition can assist in establishing a PAN material that is melt processible. If the glass transition temperature (T_g) of the starting material could be lowered without altering the copolymer composition, the viscosity would also be lowered and the material could be processed at a lower temperature. This would have a reducing effect on the kinetics of cyclization, potentially facilitating melt processing of the precursor with minimal degradation.

With the knowledge of carbon dioxide and how it affects certain polymers and their melt viscosities, it stands to reason that the amount of CO_2 used would be of interest as well. Therefore, the feasibility of melt spinning carbon fiber precursors using absorbed CO_2 can be initially evaluated by establishing the design equations for spinning of the precursor melt containing absorbed CO_2. The design equations are used to estimate the feasibility of developing a pressurized step-down chamber that prevents bubble nucleation and foaming of the precursor fiber melt at the capillary exit of the extruder. The design equations involve coupled partial differential equations describing the momentum, heat and mass transfer of the spinning and drawing of the fiber, as well as the necessary constitutive equations. Foaming is another problem that must be circumvented. However, it is possible to evaluate another avenue to control bubble growth and to see if the melt spinning of CO_2 plasticized PAN copolymer fibers are suitable for textiles and carbon fiber precursors. The versatility of carbon fibers is still evolving.

There are commercially produced polymers that have the desired qualities for great mechanical properties and would show desirable mechanical behavior. These polymers have a high mole percent of AN and show remarkable melt stability. There are a couple of commercial resins produced by BP/Amoco. The first of these is Barex, an extrudable grade AN/MA copolymer, containing 65 mol% AN, 25 mol% MA and 10 mol% elastomer. Barex is currently used for production of barrier films, and is available in 50 kg quantities. The second resin is an extrudable grade 90/10 mol% AN/MA copolymer named Amlon, also produced by BP/Amoco. Amlon was developed as a melt processable AN precursor containing less than one mol% of a stabilizer, but is no longer produced. Fortunately, a small quantity (roughly 100 g) of the copolymer was obtained for our measurements.

Barex was an ideal resin to establish a framework for the ability of CO_2 to be absorbed by and plasticize AN copolymers. This resin facilitated experimental analyses at elevated temperatures (above the T_g of the copolymer) for noteworthy lengths of time with minimal degradation. The Amlon resin provided a copolymer with a relatively high AN content that was melt stable, again suitable for time consuming, high temperature experimental measurements.

Carbon Fiber History

Carbon fiber development over the years has been difficult and rewarding. Carbon fiber is a material that demands attention in many arenas because of its high specific strength and modulus relative to other currently available engineering materials. Some of the most desirable aspects of carbon fibers are that they are chemically inert, except during extreme oxidizing conditions or when in contact with some molten materials. The fibers contribute to low creep and fatigue resistance in composite materials as well as displaying excellent damping and very good thermo-physical properties.

Carbon fibers can be used in different forms to reinforce lightweight thermosetting or thermoplastic organic materials like epoxy resins, polyesters, or polyamides. For example, short or continuous yarns, fabrics, etc. can be used to contribute stiffness and strength, and reduce the thermal expansion coefficient in the composite.[37]

High-performance carbon fiber development started in the 1950's when Union Carbide, now Cytec Fiberite, developed a process that produced high modulus fibers by hot stretching of the isotropic pitch-based carbon fiber during heat treatment at the graphitization temperature.[38] Later, Shindo[39] in Japan and Watt in the U.K., [40] working independently, created carbon fibers from polyacrylonitrile (PAN) precursor fibers. This "black orlon" was prepared from the commercial acrylic fiber that was transformed into high strength carbon fibers by heating it to 200 °C for many hours in air, followed by pyrolysis in a flame. A major problem was that the exothermic oxidation reaction to cyclize the fiber needed to be controlled. Watt and Johnson subsequently produced a fiber carbonized at 1000 °C, with a modulus of 150 GPa, which became

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[37] Lee, S. M. *International Encyclopedia of Composites*; VCH: New York, 1990-91; Vol. 1.
[38] Bacon, R.; Smith, W. H. *2nd Conf. Ind. Carbon and Graphite, Soc. Chim. Ind.* **1965,** *203*.
[39] Shindo, A. Report No. 317 Govt. Ind. Res. Instt. Osaka **1961**.
[40] Watt, W.; Phillips, L. N.; Johnson, W. *Engineer London* **1986,** *221*.

even higher after further heating at 2500 °C. During the early batch process, the need to restrict the fibers during the oxidation step was met in development of a continuous process, which featured spinning under tension. By 1966, a full-scale continuous process for converting PAN fiber precursors into carbon fibers was used at Morganite Limited.[41]

The simpler fabrication process and the lower cost in the PAN precursor received immediate attention because the PAN process for carbon fibers was more economical than the rayon (regenerated cellulose) based process. The rayon process used textile grade fibers that were subjected to complicated pyrolysis techniques to obtain a fiber with a carbon yield of only 20%.[26] The PAN process improved carbon fiber yields (50%) relative to the rayon process and did not require the expensive and difficult high-temperature orientation. The PAN precursor needed for high performance had to have a preferred orientation, but stretching the fiber when it was still relatively thermoplastic sufficed. The orientation helped to compensate for the shrinkage when the fiber was cyclized into the more stable infusible acrylic fiber when heat-treated in air at 200 °C. Further carbonization, at 1200-1400 °C, of the stabilized fiber helped to increase the tensile strength to about 3.0 GPa and the modulus to about 250 GPa. Further post-carbonization at 2500 °C improved the modulus to 350 GPa, but decreased the tensile strength.

The process development in the carbon fiber industry could, in principle, be applied to lightweight automobile parts that would reduce energy consumption. Therefore, many types of precursors are under investigation to test the feasibility for a large-scale economical production route to carbon fibers.[42,43,44,45,46,47]

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[41] Bansal, R. C.; Donnet, J. B. *Carbon Fibers 2nd Ed.*; Marcel Dekker Inc.: New York, 1994.

[42] Bhanu, V. A.; Wiles, K. B.; Banthia, A. K.; Mansuri, A.; Sankarpandian, M.; Rangarayan, P.; Glass, T. E.; Baird, D. G.; Wilkes, G. L.; McGrath, J. E. *Polymer Preprints* **2001,** *42*, 663.

[43] Bhanu, V. A.; Wiles, K. B.; Rangarayan, P.; Baird, D. G.; McGrath, J. E. *SAMPE Proceedings* **2001,** *33*, 1499.

[44] Bhanu, V. A.; Rangarayan, P.; Wiles, K. B.; Bortner, M.; Sankarpandian, M.; Godshall, D.; Glass, T. E.; Banthia, A. K.; Yang, J.; Wilkes, G. L.; Baird, D. G.; McGrath, J. E. *Polymer* **2002**, *43*, 2699-2709.

Carbon fibers may have different classifications, such as fibers with enhanced physical properties. However, there are several dimensions to this innovative and desirable fiber. Several aspects of carbon fiber are given in Table 4.

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[45] Rangarayan, P.; Yang, J.; Bhanu, V. A.; Godshall, D.; Wilkes, G. L.; McGrath, J. E.; Baird, D. G. *J. Appl. Polym. Sci.* **2002,** *85*, 69-83.

[46] Wiles, K. B.; Bhanu, V. A.; Pasquale, A. J.; Long, T. E.; McGrath, J. E. *Polymer Preprints* **2001,** *41*, 608; J. Poly. Sci, in press 2002.

[47] Yang, J.; Banthia, A. K.; Godshall, D.; Rangarayan, P.; Wilkes, G. L.; Baird, D. G.; McGrath, J. E. *Polymer Preprints* **2000,** *41*, 59.

Table 4: Moduli of different types of carbon fibers.[48]

UHM Type	Carbon fibers with modulus greater than 500 GPa.
HM Type	Carbon fibers with modulus greater than 300 GPa and with a tensile-strength and tensile to modulus ratio of less than 1%.
IM Type	Carbon fibers with modulus up to 300 GPa and with a strength to modulus ratio above 1x10-2.
Low Modulus Type	Carbon fibers with modulus as low as 100 GPa and with low strength. Carbon fibers that have an isotropic structure.
HT Type	Carbon fibers with tensile strength values greater than 3000 MPa and strength to stiffness ratio between 1.5 and 2x10-2.

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[48] Donnet, J. B.; Bansal, R. C. *Carbon Fibers*; Marcel Dekker Inc.: New York, 1990.

High strength carbon fiber composites are revolutionary. However, they are mainly employed in *high tech* applications, e.g. aerospace and military. If the cost could be reduced this would allow for an expansion of carbon fibers to be used in the automotive industry.[49] It is important to briefly discuss the basic chemistry that is currently used to develop carbon fibers and their melt processible precursor. This process can be amended to develop a more cost-effective carbon fiber.

Some of the more commonly used carbon fibers are acrylic fibers. These fibers are widely used in the textile industry.**[50]** Acrylic fibers are copolymers of acrylonitrile (AN) with about three mol % of other comonomers. The comonomers include 3 – 4 mol % of methyl acryl ate (MA), vinyl acetate etc., which promote solubility in commonly used fiber-spinning solvents like DMF, and 1-2 mol % of acidic comonomers like acrylic acid or itaconic acid,[2,**51**] which positively aid in the dyeing the fibers. A delicately controlled thermal treatment brings about the metamorphosis of these textile fibers into carbon fibers.[3] The significant steps in this process are termed *stabilization and carbonization.*

Oxidation of PAN, which is part of a higher order process of making carbon fiber, has several requirements. For decisive carbon fiber production, high tenacity of acrylic precursor, low level of comonomer, and smaller tow sizes are important attributes. A company by the name of Stackpole, which is a U.S. company, has some uses for developing the carbon fiber precursor such as flame-retardant textile material and in breaking systems, but serves primarily as a precursor for high strength carbon fiber.

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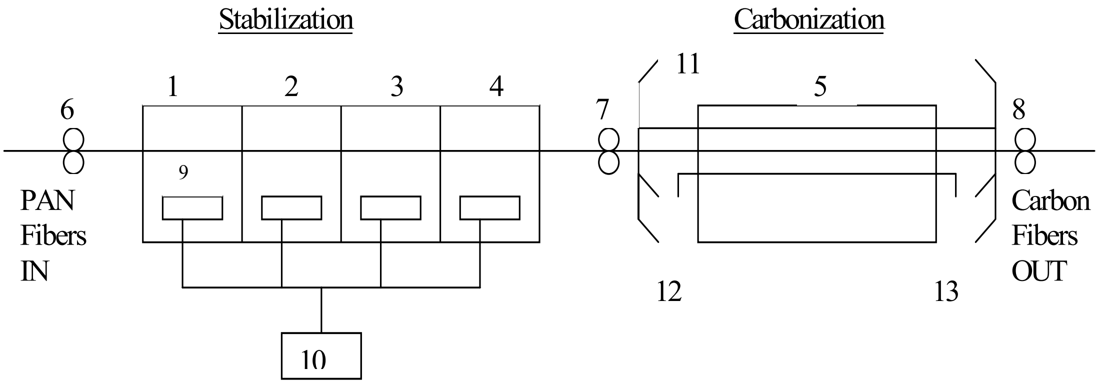
[49] Tullo AH., *Chemical & Engineering News* 2000;August 28:11.

[50] Bahl OP.in Donnet JB, Wang TK, Rebouillat S, Peng JCM. Eds. Carbon Fibers, 3rd ed. New York: Marcel Dekker; 1998.

[51] Peebles LH. Carbon Fibers: Structure and Formation, New York: CRC Press; 1995.

PANOX is a polyacrylonitrile that has been oxidized; this is a trade name for a product mad by R. K. Carbon Fibers in the United Kingdom. PANOX can be processed as a stretched-broken tow or cut to staple, the acrylic precursor may be a tow of 1.5 dpf 480 K total denier. A Courtelle tow, which contains itaconic acid units that provide the necessary reduction in the onset temperature and the magnitude of the exotherm during the oxidation step, is crucial in developing the desired effect for carbon fiber.[2]

The oxidation of PAN takes place in an air atmosphere at temperatures ranging from 200 to 300 °C. The tow passes through an oven (Fig. 4), with the temperature increasing in each region slowly to achieve the desired fiber. The time required for this process is about 2.25 hours. During this process the air is continuously exhausted to remove the volatiles. The polymer goes through cyclization via the pendant nitrile groups, cross-linking through nitrile reaction with methane hydrogens, oxidation to produce peroxides and ketones, and scission reactions which can lead to carbon-carbon double bonds.[2] This will be explained in greater detail later along with how to produce carbon fiber via new processing criteria.



8. Stabilization Oven
9. Stabilization Oven
10. Stabilization Oven
11. Stabilization Oven
12. Carbonization Furance
13. Feed Rollers

1. Pinch Rollers
2. Pinch Rollers
3. Heating Mantle
4. Temperature Controller
5. Reaction Vessel
6. Nitrogen Gas In
7. Nitrogen Gas In

Figure 4: A schematic drawing of the stabilization and carbonization for carbon fiber.

During the stabilization step, the polymer is usually heated at 200-250 °C for 5-10 hours (times may vary) in the presence of air. As a result, the polymer containing predominantly AN units is converted from a linear structure to a ladder-like structure via the intramolecular cyclization of pendant nitrile groups and intermolecular crosslinking. This process is believed to occur both intra- and inter- molecularly, and competes with the polymer degradation and crosslinking reactions that take place simultaneously.[35] An acceptable yield and quality of product (stabilized fibers) is achieved by operating at the right temperature and amount of oxygen.[35, 36] The next step requires that the stabilized fibers are carefully heated in an inert environment at >1000° C for a few hours to remove all the non-carbon elements and to obtain a carbon fiber with 97% carbon content. Therefore, this step is characterized as *carbonization*.

Carbon fibers are judged on their carbon content, which influences mechanical properties such as the tensile modulus.[34, 35] The textile fibers are spun out from relatively dilute solutions at mild temperatures. The solvent allows (i) use of low spinning temperatures that retard premature cyclization or crosslinking, (ii) formation of very fine fibers with a uniform diameter on the order of 20 microns, which is necessary for successful stabilization, and (iii) overcoming the pseudo crystallinity present in these high acrylonitrile-containing fibers.[2]

Carbon fiber is known for its superior qualities, but many things must align to produce a viable fiber with the mechanical qualities that are desired. The microstructure of fibers can be arranged in different morphologies, some of which can affect the mechanical behavior. Early work by Diefendorf and Tokarsky[52] indicated that the macrostructure of PAN-based carbon fibers, similar to that of many other synthetic precursor fibers, is fibrillar. However, when a cross-section was studied, there were variations that influenced fiber performance.

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[52] Diefendorf, R. J.; and Tokarsky, E.: *Polym. Eng. Sei.,* vol. 15, no. 3, 1975, pp. 150-159.

The shape of the fiber can also influence a PAN fiber's ability to perform. Carbon fibers, similar to other fibers, also appear to display different properties when circular fibers are compared with noncircular fibers. Because they are formed by precipitation, the cross-sectional shape of solution-spun PAN fiber tends to be either circular or dogbone. The modulus and strength for these two shapes of PAN-based carbon fibers are quite different, although the trends are similar, as determined by Diefendorf and Tokarsky.[37] The same trends were also found in other studies.[53, 54]As the modulus of a dogbone fiber increases, so does its strength. When the modulus increases above 250 GPa, the strength of a round fiber actually begins to decrease.[55] This decrease may be related to flaw-inducing impurities in the fiber,[56] differences in the flaw sensitivity of the fiber, or differences in residual stresses.[37]

Changing the shape and microstructure can change the mechanical properties of a fiber. The effect of these two variables is difficult to separate. However, fibers with noncircular cross sections have long been used in the synthetic fiber industry to improve the wetting characteristics and increase the buckling resistance of polymeric fibers. During 1989, Owens-Coming Fiberglass Corporation introduced a variety of glass fiber with a trilobal cross section, claiming that the shape resulted in a significant improvement in fiber stiffness as well as tensile strength.[57] The noncircular fibers are superior when used for composite applications.

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[53] Le Maistre, Christopher William: The Origin of Structure in Carbon Fibers. Ph.D. Diss., Rensselaer Polytechnic Inst., 1971.

[54] Tokarsky, E. W.: The Relationships of Structure to Properties in Carbon Fibers. Ph.D. Diss., Rensselaer Polytechnic Inst., 1973.

[55] Johnson, John W.: Factors Affecting the Tensile Strength of Carbon-Graphite Fibers. *Appl. Polymer Symp.,* no. 9, 1969, pp. 229-243.

[56] Reynolds, W. N.; and Moreton, R.: Some Factors Affecting the Strengths of Carbon Fibres. *Philos. Trans. Royal SOC. London,* ser. A, vol. 294, no. 1411, Jan. 21, 1980, pp. 451461.

[57] Kaverman, Richard: New Shapes Give Glass Fibers More Strength. *Res. & Dev.,* Mar. 1989, p. 20.

Pitch-based carbon fibers are melt-spun. They can be extruded into a variety of cross-sectional shapes merely by changing the shape of the extrusion die.[58] To create these trilobal fibers, a solvent-extracted mesophase is extruded through the trilobal spinnerette capillary, producing fibers with a trilobal cross section. When heat-treated at 1900 °C, the tensile strength of the noncircular fibers were 39% higher than round fibers of equal cross section that were produced for comparison. Because the microstructure of the trilobal fibers is different from the radial microstructure seen in the round fibers, it is difficult to tell if the increased strength is the result of the change in fiber shape or the change in microstructure. The investigators noted that this increase in strength could be caused by several factors, including the possibility that the residual trilobal fibers might have decreased surface flaws compared to round fibers, thus making them stronger.

The Gainer group melt-spun[59] a heat soaked mesophase into a trilobal fiber using similar extrusions methods. They found that due to the more trilobal shape these fibers were noncircular to a greater degree than those produced by Edie. The trilobal fibers were compared with round fibers of equal cross section, then carbonized at 1900 °C. The two fiber shapes were tested and the trilobal fibers out-performed the round fibers of equal size (27 μm diameter) by about 27%.[60] While both failed, the trilobal revealed fewer flaws, thus contributing to the superior quality.
BASF Structural Materials, Incorporated, began producing PAN-based carbon fibers using a new melt-spun precursor technology.[61] In this process, the acrylonitrile was polymerized in an aqueous suspension, eliminating the need for an organic solvent. After the PAN was purified and

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[58] Edie, D. D.; Fox, N. K.; Barnett, B. C.; and Fain, C. C.: Melt-Spun Non- Circular Carbon Fibers. *Carbon,* vol. 24, no. 4, 1986, pp. 477482.

[59] Gainey, H. E.; Handlos, **A.** A.; Edie, D. D.; Kennedy, J. M.; and Fain, C. C.: Flaw Distributions in Noncircular Carbon Fibers. *FIBER-TEX 1988,* John D. Buckley, ed., NASA CP-3038, 1989, pp. 163-167.

[60] Buckley, J.D.; Edie, D.D.Carbon-Carbon Materials and Composites. William Andrew Publishing/Noyes. (1993).

[61] Daumit, G. P.; and KO, **Y.** S.: A Unique Approach to Carbon Fiber Precursor Development. *High Tech-The Way Into the Nineties,* K. Brunsch, H. D. Golden, and C. M. Herhert, eds., Elsevier Science Publ. B. V. (Amsterdam), 1986, pp. 201-213.

the water removed, it was compounded, pelletized, and fed to an extruder. When melted in the extruder, the pellets, plasticized with excess water, formed a homogeneous melt that could be extruded into fiber form. During extrusion the excess water was driven off, allowing the PAN precursor fiber to solidify. The advantage of this process compared with standard solution-spinning technology is eliminating the need for solvent recovery and decoupling the polymerization step from the spinning step. Another advantage is that large amounts of residual solvent do not have to diffuse out of the fiber during solidification, which yields a more uniform structure. Since the fibers are melt-spun, the fiber shape can be controlled more efficiently.

The microstructure of the polymeric precursor fibers used to form PAN-based carbon fibers is fibrillar, but mesophase precursor fibers are composed of extended domains of a highly oriented structure. To a large extent, the final microstructure of the carbon fiber replicates that of the precursor fiber. In PAN-based and rayon-based carbon fibers the graphite crystallites are arranged into a fibrillar substructure, whereas pitch-based carbon fibers have an extended graphitic layer structure. These larger regions of graphitic structure allow pitch-based carbon fibers to display extremely high moduli; this structure also makes pitch-based carbon fibers more flaw-sensitive, which accounts for their lower tensile strengths. Modifying the flow profile during fiber extrusion results in a significant change in the microstructure. These changes can form new microstructures in pitch-based fibers, thus improving both the tensile strength and compressive strength.

The most cost-effective and environmentally friendly method of forming carbon fibers is to develop a procedure that would eliminate the use of solvent spinning and promote the use of melt spinning, which has been adopted by various research groups including our own laboratory.[10, 28, 62, 63] Melt spinning processes demand precursors with high thermal stability. However, this could result in the loss of some mechanical properties.[27] It is a daunting task to reduce the cost of carbon fibers[64] not only due to the delicate balance between thermal stability and mechanical properties, but also because the chemistry for processible precursors is dimly understood. Therefore, there is a need to study the design of the melt processible carbon fiber precursors, with the objective of achieving reasonable thermal stability without losing important mechanical properties. It has been noted in studies from our laboratory that copolymers containing >90 mol% AN do not truly melt, and therefore exhibit very high melt viscosity.[28,65] Copolymers containing 85-90 mol% AN have a melt viscosity in the processible range of 100-1000 Pa-s at 220 ^{o}C, beyond which they thermally degrade.[30] Increasing the MA comonomer content (10-15 mol%) reduces the melting point and influences the cyclization of the nitrile groups responsible for the stabilization process. As a result, addition of MA comonomer lowers mechanical properties slightly. This lower amount of AN promotes fiber fusion during the stabilization step rather than cyclization or cross-linking. To alleviate this problem it was thought to be worthwhile to marginally cross-link the fibers.[66] Therefore, a UV-sensitive comonomer was carefully selected to afford a terpolymer precursor having reasonable mechanical strength prior to stabilization.

Herein, the design and synthesis of AN terpolymers containing MA as the major comonomer and acryloyl benzophenone (ABP, <1 mol%) as the minor comonomer needed for

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[62] Bhanu VA, Wiles KB, Bortner M, Glass TE, Godshall D, Baird DG, Wilkes GL, McGrath JE. Polymer Preprints **2002**, *43(2)*, 1017-1018.

[63] Bhanu VA, Wiles KB, Rangarajan P, Glass TE, Godshall D, Sankarpandian M, Baird DG, Wilkes GL, Banthia AK, McGrath JE. Polymer Preprints **2001**, *42(2)*, 595-596.

[64] Bhanu VA, Wiles KB, Bortner M, Godshall D, Glass TE, Baird DG, Wilkes GL, McGrath JE. Polymer Preprints **2002**, **43(1)**, 674-675.

[65] Godshall D, Rangarajan P, Baird DG, Wilkes GL, Bhanu VA, McGrath JE. Polymer **2003**, *44(5)*, 4221-4228; Godshall D. Ph D Dissertation, Virginia Polytechnic Institute and State University, USA, 2003

[66] Guillet J. Polymer Photophysics and Photochemistry, Cambridge: Cambridge University Press; 1985; Paiva MC, Kotasthane P,Edie DD, Ogale AA. Carbon **2003**, *41*, 1399-1409.

assisting in the UV-induced cross-linking.[67] The choice of the major comonomer was based on a study of the reactivity ratios of AN and MA, which showed that these monomers make an excellent pair for copolymerization.[68] Emulsion polymerization was chosen as the route for synthesis after a systematic study of possible polymerization methods in our laboratory.[40,69,70] Structural characterization and thermal analysis of the copolymers are reported. Both dynamic and steady shear viscosities have been studied to assess the stability of these copolymers as melt-processible carbon fiber precursors.

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[67] Mukundan T, Bhanu VA, Wiles KB, Bortner M, Baird DG, Wilkes GL, McGrath JE. Polymer Preprints **2003**, *44(2)*, 651-652.

[68] K.B. Wiles, V.A. Bhanu, A.J. Pasquale, T.E. Long, and J. E. McGrath, "Monomer Reactivity Ratios for Acrylonitrile-Methyl Acrylate Free-Radical Copolymerization," *Journal of Polymer Science: Part A: Polymer Chemistry*, **2004**, *42*, 2994-3001; Wiles K.B. MS Thesis, Virginia Polytechnic University and State University, USA, 2002.

[69] Bhanu VA, Wiles KB, Bortner M, Godshall D, Glass TE, Baird DG, Wilkes GL, , McGrath JE. Polymer Preprints **2002**, *43(1)*, 674-675.

[70] Bhanu VA, Bortner M, Mukundan T, Glass TE, Baird DG, McGrath JE.Polyme Preprints **2003**, *44(1)*, 1067-1068.

Chapter III: Experimental

Materials

Acrylonitrile (AN, 99+%), which contained monomethyl ether hydroquinone (45 parts per million) as an inhibitor was purchased from Aldrich. The inhibitor present in the monomers had to be removed with an activated alumina column. Since AN is a known cancer-causing agent, extreme caution was exercised when handling and disposing of it in order to reduce the risk of contact and ground water contamination. The methyl acrylate (MA, 99%) also contained inhibitor (100 parts per million of monomethyl ether hydroquione), and was purchased from Aldrich. The inhibitor was removed with an activated alumina column. After the removal of the inhibitors the monomers were then stored in a refrigerator until needed to prevent any premature polymerization of the monomers. 1-Dodecanethiol (DOSH), which is the chain transfer agent (CTA), and boric acid were purchased from Aldrich and used as received. Acryloyl benzophenone (ABP) was synthesized using a reported procedure.[71] Additional ABP was purchased from Monomer-Polymer & Dajac Labs, Inc. of Feasterville, PA as well. DOWFAX 8390 solution surfactant was obtained from the Dow Chemical Company. Ammonium persulfate (APS), which was the initiator, and magnesium sulfate ($MgSO_4$) were purchased from EM Science and were used as received.

Polymerization

The copolymer and terpolymer synthesis was carried out in aqueous medium via an emulsion polymerization route. In a typical reaction, a 250 mL reaction flask fitted with a condenser, glass stirrer, nitrogen inlet tube and thermocouple probe was purged with nitrogen and was charged with 50 mL water containing the surfactant (2.07 g, 3.46 mmol) this mixture

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[71] Carlini C, Gurzoni F. *Polymer* **1983**, *24*, 101.

was maintained at a temperature of 57 ºC for 15 minutes. A premix of the monomers (2.5 mL, 10 % of the total, 37.9 mmol AN and 5.23 mmol MA) and the DOSH (0.50 g, 2.5 mmol) was added via an addition funnel. About 5 mL from the addition funnel was added to the reaction flask, followed by the initiator (17 mg in 10 mL water, 0.074 mmol). The temperature was raised to 60 °C and the remaining monomer mixture (AN, 20.5 g, MA, 5.48 g and ABP, 1.15 g) was added drop-wise over a period of two hours. Following complete addition of the monomer mixture, an additional quantity of initiator (10 mg, 0.044 mmol in 10 mL water) was added to the reaction flask. The latex was maintained at 60 ºC for 30 minutes. The product was isolated by precipitation in 500 mL of a 1% aqueous solution of $MgSO_4$ at 65 °C in a blender. The terpolymer was vacuum dried at 70 °C for 24 hours (recovered yield: 85 %).

Synthetic Variables

The variables that were selected in the copolymerization reactions were CTA, APS, and Dow Fax. The AN/MA copolymers were synthesized using the same methods as described previously. The only exception was that various amounts of the CTA, APS, and DowFax were employed. The objective of this study was to determine how these synthetic variables could affect copolymer and terpolymer behavior. There was a series of three samples for each of the selected variables ranging from low, medium and high. Each of these syntheses was carried out in a series of three while keeping the other variables and conditions constant. This was done to investigate how these conditions could enhance polymerization of the co-and terpolymers. The terpolymer of AN, MA, and ABP was polymerized using the same techniques as previously described.

Isolation of Copolymers

The copolymers and terpolymers were precipitated in 500 mL of a 1% aqueous $MgSO_4$ solution in order to recover the polymers in good yield. Extremely careful techniques were used so as to minimize the loss of any solution or polymer during the isolation process. A 1200-mL blender was used to stir the water while the copolymer solution was added drop-wise to the agitated water. The solution was added slowly to the aqueous medium and the reaction flask was rinsed with deionized water until the entire residual polymer was in the blender. This process was repeated until no solution was left in the flask. The copolymer was filtered from the aqueous solution by vacuum filtration through a Buchner funnel. Another 500 mL of water was heated to a temperature of 65 ºC where the polymer cake was allowed to remain for 30 minutes, and then vacuum filtered through previously stated techniques. The polymer was allowed to remain under vacuum for about 5-10 minutes longer. The aqueous monomer solution was discarded and care was taken to prevent ground water contamination. The filter paper that was used in the Buchner funnel was pre-weighed so that the copolymer percent yield could be accurately calculated. The copolymer and the filter paper were placed in a large crystallizing dish and dried in a vacuum oven at temperatures up to 70 °C for 24 hours. The temperature is crucial to allow the water to diffuse out of the copolymer. The copolymer and paper filter were removed from the oven and allowed to cool to room temperature. The copolymer and the filter were then weighed and the weight of the paper filter was subtracted from the total weight of the copolymer and filter in order to determine the copolymer yield. The copolymer was stored in a 250-mL amber bottle.

Stabilization with Boric Acid

The primary function of the thermal stabilization step is to stabilize the carbon fiber precursor so it is thermally stable during further heat treatment steps. The addition of 2% by weight of boric acid to the co-and terpolymer is a beneficial in this process. The boric acid aids in melt stability of the carbon fiber precursor. The exact mechanism by which boric acid assists in this process is not clear.

The method used for stabilization and carbonization of melt-spun fibers was as follows: the as-spun fiber tows were clamped in a metal frame to maintain a constant length and then UV irradiated in 100 W Oriel Hg arc lamp for 3 hours at 110 °C. Next, the fibers were oxidatively stabilized in a forced-circulation oven (ATS 3610) at 320 °C and 30 min soak time using a heating rate of 2.5 °C/min. Oxidatively stabilized fibers were then carbonized at 1500 °C in He atmosphere in an Astro Furnace.

The as spun precursor fiber structure was crosslinked so that orientation would not be lost and extensive chain relaxation and chain scission would not occur during carbonization.[10] The stabilization reaction is the rate limiting step of the PAN-based carbon fiber production process, and a great deal of effort has been put forth to accelerate this process.[72] Although the stabilization has been mentioned previously, it is imperative that it is discussed in more detail to make a complicated process clear.

Following the prestretching process, carbon fiber precursors are heated to suitable temperatures (220-280 °C) for stabilization. During this process, an exothermic cyclization reaction leads to the formation of a ladder polymer, which is promoted by the pendant nitrile groups in the polymer chain. A commercial PAN stabilization oven heats the fibers while they are kept under tension during the stabilization process to maintain alignment of the PAN polymer. Otherwise, relaxation occurs and the resulting ladder polymer loses orientation with respect to the fiber axis. Formation of the ladder polymer results in significantly enhanced

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[72] Jain, M. K.; Abhiraman, A. S. *Journal of Materials Science* **1987**, *22*, 278-300.

thermal stability, easily facilitating heating to higher temperatures for carbonization.[2] Cyclization that occurs in the thermal stabilization reaction could be quite undesirable if attempting to melt spin such precursor materials at elevated temperatures. It is important to understand the role of the factors that strongly influence the crosslinking/stabilization reaction when assessing the feasibility of melt extrusion of acrylic copolymers. Understanding the influence of the nature of the comonomer incorporated into the precursor is crucial, as is the molecular weight of the precursor itself, the AN content of the precursor copolymer, and the atmosphere in which the stabilization reaction takes place. These variables, when optimized, will facilitate the tailoring of a suitable precursor material for melt extrusion into carbon fiber precursors.

Powder precursors were compressed at 25 °C to obtain 1 mm thick disks using a pelletizing die and a Carver laboratory press. Pelletized precursors were packed in the barrel of an Instron capillary rheometer 3211 fitted with a die of 250 μm diameter and an aspect ratio of about 2 for melt spinning at a temperatures ranging from 200-210 ^{o}C. The nominal shear rate during spinning was approximately 500 and about 1500 s^{-1} for low and high throughput rates of 0.04 and 0.14 cm^3/min, respectively. Spun fibers were collected on a spool at a winding speed of 125-300 m/min; the nominal draw down ratio was in the range of 40-310.

Dr. V.A. Bhanu, Dr. T. Mukundan and the author synthesized a series of copolymers that were designed to develop a low cost alternative to melt processing carbon fibers. There were many copolymers created and studied. The polymerization batch was usually 5-10 g, and a suitable polymerization technique, comonomers, copolymer molar composition, and molecular weight were identified. Later, Monomer Polymer Inc.of Feastersville, PA was able to scale-up of the recipe that was developed in our laboratory. A 85/15 mol % AN/MA copolymer was synthesized, and the other samples were 85/14/1 mole % AN/MA/ABP terpolymers. The typical reaction batch was about one kg, and four separate batches were synthesized.

Intrinsic viscosities were measured using a Cannon Ubbelhode viscometer at 25 ^{o}C. Absolute molecular weight measurements from gel permeation chromatography (GPC) were obtained at 60 ^{o}C with a Waters 2690 Separation Module equipped with a differential refractometer detector and an online differential viscometric detector (Viscotek T60A) coupled in parallel. NMP containing 0.2 M P_2O_5 was used as a solvent.

A typical Gaussian MWD was observed for the 85/15 AN/MA copolymer and the 85/14/1 AN/MA/ABP resin 2 and resin 3 terpolymers. However, the resin 1 terpolymer has a high MW tail in the MWD, and also had a significantly higher M_w and M_n than the other three scaled up resins. This particular resin degraded before flowing when attempting to measure the rheological properties, and as a result was not used to any significant degree in this work. The other three resins have similarly narrow MWDs (1.7-2.5), but varying molecular weights (M_w from 27,300-65,900 g/mol) and IV (0.36-0.52). These three resins were a culmination of experimental screenings. This provided an avenue for great a deal work. Three other AN/MA copolymers, containing 93, 95, and 98 mol% AN, were used for identification of the effects of AN on the ability to absorb CO_2.

Mechanical Behavior

Shear rheological measurements were used to identify the small amplitude dynamic oscillatory rheological properties, as well as the steady shear flow properties at low shear rates ($\gamma < 10$ s^{-1}) of the AN-containing resins. A Rheometrics RMS800 with 25.0 mm parallel plate fixture was used to obtain this information. The reason for this procedure was to establish some shear rheological data before degradation. This was done to study the melt stability of the resins that were prepared in our laboratory.

Powdered samples were compression molded into circular disks of 25.0 mm diameter and 1.0 mm thickness using a press at room temperature. The Amlon copolymer was compression molded into circular disks of the same dimensions at 210 °C. Barex was compression molded into disks at 180 °C.

During loading, heating, and equilibration of the samples in the rheometer, an inert nitrogen atmosphere was used in the rheometer oven. The presence of oxygen has been shown to accelerate the crosslinking reaction, and use of an inert atmosphere helped to prevent significant degradation prior to rheological measurements.[73] The samples were loaded into the hot rheometer and allowed to equilibrate for five minutes preceding data acquisition. Five minutes was found to be the minimal amount of time for (relative) temperature equilibration in the rheometer oven.

During the course of the project, torsional rheometry was used to screen the copolymers. In particular, the steady shear viscosity (0) increase was monitored as a function of time. The results of the rheological studies provided feedback regarding 0 levels and their magnitude of increase as a function of time. This feedback screening process narrowed the synthetic and experimental polymerization variables.

Tensile Testing of Fibers

Tensile properties of the fibers at various stages of treatment were measured in a computerized MTI Phoenix tensile testing instrument equipped with 500 g load cell (ASTM D 3379-75).

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[73] Ehrburger, P.; Donnet, J. B. *Handbook of fiber science and technology:* Volume III, high technology fibers; M. Dekker: New York, **1983**; Chapter 5, pp 169-220.

Scanning Electron Microscopy (SEM)

SEM micrographs of the fibers were obtained using a Hitachi Cold Field Emission Scanning Electron Microscope (CFE-SEM) S-4700. Specimens were Pt sputter coated to avoid charging.

Characterization

The IR spectrum was recorded using a Nicolet FTIR spectrometer. The intrinsic viscosity (IV) measurements were performed in N-methyl pyrrolidone (NMP) at 25 °C using a Cannon Ubbelohde viscometer. The melt viscosity was measured using an RMS 800 Dynamic Spectrometer. A steady shear frequency sweep was employed to determine the melt viscosity, and a time sweep was used to determine the stability of the polymer melt over a time of 30 minutes at 220 °C. Differential scanning calorimetry (DSC) was used to determine the glass transition temperature (T_g) of the copolymers with a TA Instruments model Q 1000. The scans were carried out under nitrogen, with a heating rate of 10 °C/ min and a sample mass of 5 mg. The weight-loss pattern of the tepolymer was determined using a TA Instruments model Q 500 TGA in nitrogen atmosphere at a heating rate of 10 °C/min, using a sample mass of 10 mg.

Gel Permeation Chromatograhy (GPC) Procedures

Gel permeation chromatography (GPC), often referred to as Size Exclusion Chromatography (SEC), was conducted on samples to determine the molecular weight of the copolymers that were produced. A Waters 150C ALC/GPC chromatograph was used at 60 °C. A weight of 0.02 grams of the copolymer was dissolved in NMP containing 0.02 M phosphorus pentoxide (P_2O_5). The flow of the mobile phase (NMP with 0.02 M P_2O_5) through the column was 1 mL/min and the column used was a Waters Styragel HRO.5+2+3. The flow of the mobile phase through the column contained the copolymer and the packing in the column contains different porosities that fractionate the copolymer molecules based on size. The elution time is a relative measure of the size and allows calculation of molecular weights of the copolymer via hydrodynamic calibrations. Two detectors (a refractive index detector and a Viscotek Mode 100 viscosity detector) were used in parallel to detect the copolymers as they eluted from the separation column.

Figure 7 shows the apparent molecular weight distribution peak is monomodal. The number average molecular weight of this copolymer (M_n) was determined via universal calibration[74] to be 37,000 g/mol, which indicates a high molecular weight compared to other carbon fiber precursor materials. High molecular weight was beneficial, since loss of copolymer during the precipitation and filtering processes might occur if low molecular weight copolymers were produced.

Nuclear Magnetic Resonance (NMR)

In order to determine the amount of each comonomer that was incorporated into the copolymer, proton nuclear magnetic resonance, ^1H NMR, was performed on the copolymer samples. This type of analytical technique is used to determine the amounts of each structure in a copolymer and is widely accepted and used in industry and academia at the present time for the study of polymerization kinetics.[75,76] It was important to be sure to remove any remaining monomer via washing, because residual monomer could affect the experimental results. The isolated copolymers were then dried and weighed. The weighed copolymer sample was removed and dissolved in d_6-DMSO for the ^1H NMR measurements. A JEOL USA 500 MHz NMR instrument was used in the single pulse mode to obtain the spectra at room temperature for the

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[74] Wu, C. Handbook of Size Exclusion Chromatography; Dekker: New York, 1995.

[75] Brandolini, A. J. *NMR Spectra of Polymer and Polymer Additives*; Marcel Dekker: New York, 2000.

[76] Macomber, R. S. *NMR Spectroscopy: Essential Theory and Practice*; Brace Jovanovich Publishers: New York, 1988.

copolymer samples. The use of this extremely high field instrument helped to distinguish the methyl and methylene peaks of the copolymer. Previous studies in the literature to determine the copolymer compositions produced relatively poor ^{1}H NMR spectra that contained overlapped peaks of the methyl and methylene peaks with other peaks in the spectra. Therefore, precise determination of the copolymer compositions was difficult. The use of the 500 MHz magnetic field allowed for successful resolution of the peaks and generation of a spectrum of importance. For each charge ratio that was conducted, ^{1}H NMR produced the corresponding values of each comonomer incorporated into the copolymer.[77] These mole percentages were in agreement with the theoretical values expected. ^{1}H NMR experiments produced well-resolved peaks that corresponded to the methyl group on the methyl acrylate structure and the methylene groups on both the acrylonitrile and methyl acrylate comonomers that were incorporated into the copolymer.

Thermal Analysis

Differential scanning calorimetry (DSC) was used to determine the glass transition temperatures (T_gs) of the copolymers. The T_g can be determined by several methods. It can be done by monitoring the change in physical properties as a function of temperature, which defines T_g as the beginning or the midpoint of the change in properties. The T_g is a function of heating rate as well. The physical properties that are most often monitored to measure T_g include thermal expansion coefficient, heat capacity, diffusion coefficient, and dynamic modulus, T_gs based on these measurements are known to be static measurements because the polymer is at rest during the measurements.[2] The T_g will increase with the heating rate. However, in dynamic measurements the modulus or dielectric constants are measured many times per second as the sample is being heated, and the T_g will increase with the measurement frequency.

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[77] Wiles, K. M.S. Thesis,Virginia Polytechnic Institute and State University. VA, 2002.

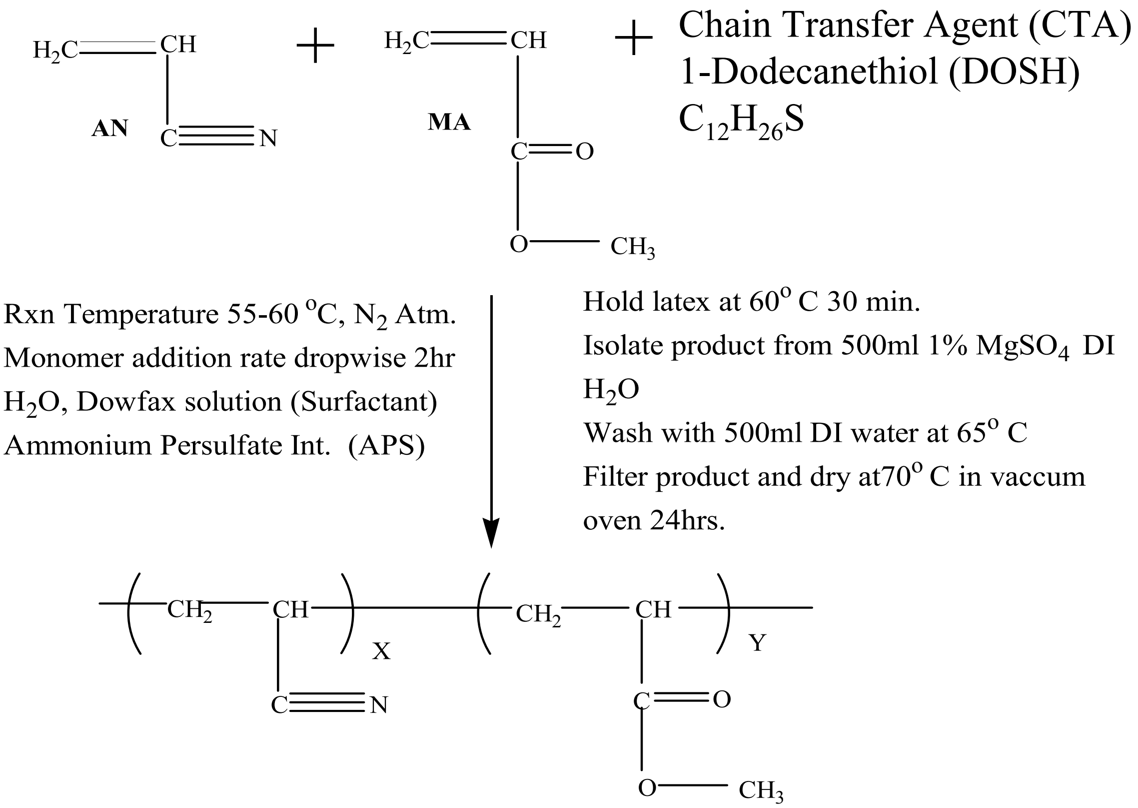
With semicrystalline polymers and fibers, the glass transition is associated with the amorphous domains, and the temperature and magnitude of the physical property changes at the transition reflect changes in the morphology. For example, if the crystallinity of a fiber is changed then the amorphous content will move in the opposite direction. Processes such as annealing and drawing increase the crystalline volume fraction, which will decrease the amorphous fraction and this will be reflected in a decrease in the change in heat capacity, modulus, and volume during the glass transition.

The glass transition temperature for PAN can be observed, but it is not just associated with amorphous domains (at least to the degree possible with more conventional semicrystalline polymers and fibers). This is consistent with the ambiguous nature of PAN morphology.

Thermo-gravimetric analysis (TGA) was employed to determine the weight loss pattern as a function of temperature. A TA Instruments TGA 2950 thermogravimetric analyzer (TGA) was used to measure the weight loss of the copolymers. A nitrogen purge of 24 mL/min and platinum pans were used. Measurements were started at room temperature (25 °C) and ramped to 250 ^{o}C at a heating rate of 10 ^{o}C/min.

Chapter IV: Results and Discussion

The reaction scheme for the copolymerization of acrylonitrile and methyl acrylate via emulsion polymerization using APS as the free radical initiator at 57 ºC is shown in Figure 5. The reaction scheme for the synthesis of the ABP termonomer is shown in Figure 6. The weight and number average molecular weights (M_n and M_w), intrinsic viscosities (IV), and polydispersity (PDI) values for the synthesized co- and terpolymers are presented in Table 5. Figure 7 shows the molecular weight distribution (MWD) data for each of these polymers. Figure 8 shows the GPC chromatogram for an 85/15 mole percent AN/MA sample in NMP containing 0.02M P_2O_5 at 60 °C.

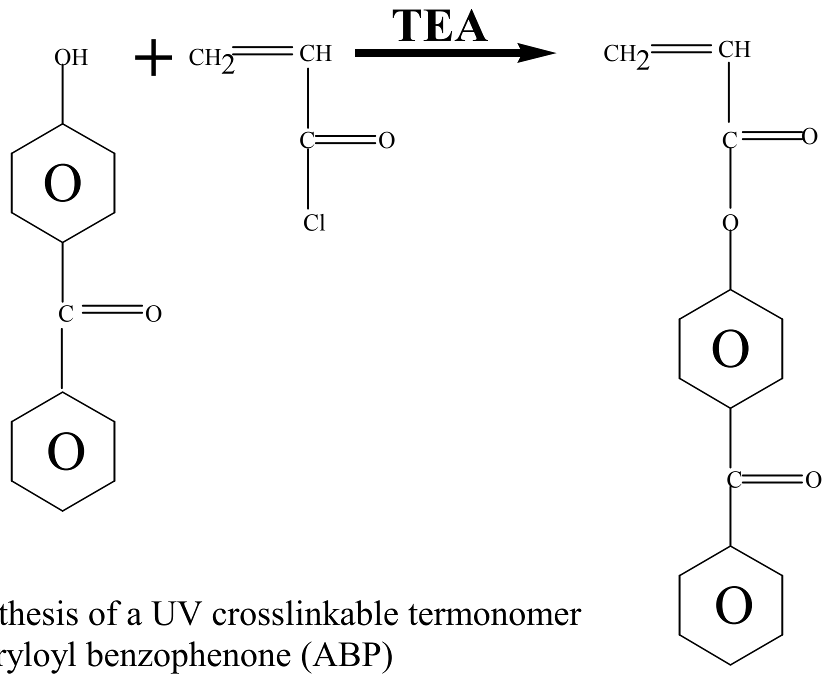


Chain Transfer Agent (CTA)
1-Dodecanethiol (DOSH)
$C_{12}H_{26}S$

Rxn Temperature 55-60 ^oC, N_2 Atm.
Monomer addition rate dropwise 2hr
H_2O, Dowfax solution (Surfactant)
Ammonium Persulfate Int. (APS)

Hold latex at 60^o C 30 min.
Isolate product from 500ml 1% $MgSO_4$ DI H_2O
Wash with 500ml DI water at 65^o C
Filter product and dry at70^o C in vaccum oven 24hrs.

Figure 5: Reaction scheme and conditions for the copolymerization of acrylonitrile and methyl acrylate.



ABP

1.Synthesis of a UV crosslinkable termonomer
2. Acryloyl benzophenone (ABP)
3. Contains a photo-active aromatic keto group
4. Acrylic monomer projected to copolymerize well and not detract from melt stability

Figure 6: Reaction scheme for the synthesis of ABP.

Table 5: Molecular weight information for the AN/MA copolymer and AN/MA/ABP terpolymers.

AN/MA molar ratio	AN/MA molar ratio (NMP/25oC)	M_n (GPC, g/mol)	M_w (GPC, g/mol)	PDI
85/15	0.50	26,500	65,900	2.5
85/14/1 batch 1	1.20	47,800	205,900	4.3
85/14/1 batch 2	0.36	16,300	27,300	1.7
85/14/1 batch 3	0.52	22,000	41,700	1.9

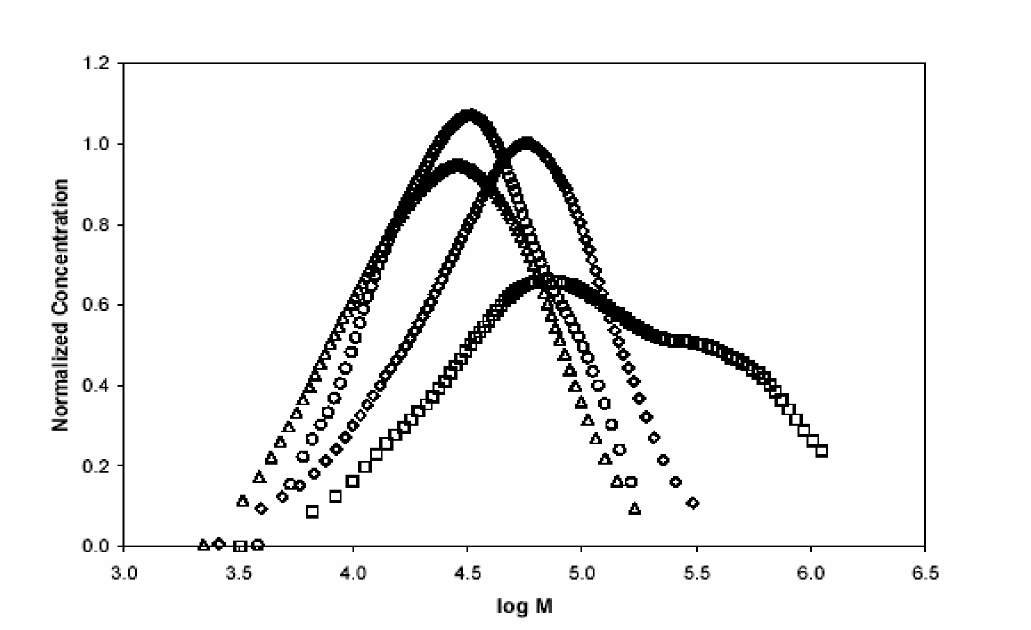


Figure 7: Molecular weight distribution for the AN/MA copolymer and AN/MA/ABP terpolymers. (◊) AN/MA copolymer; (□) batch 1 terpolymer; (Δ) batch 2 terpolymer; (o) batch 3 terpolymer

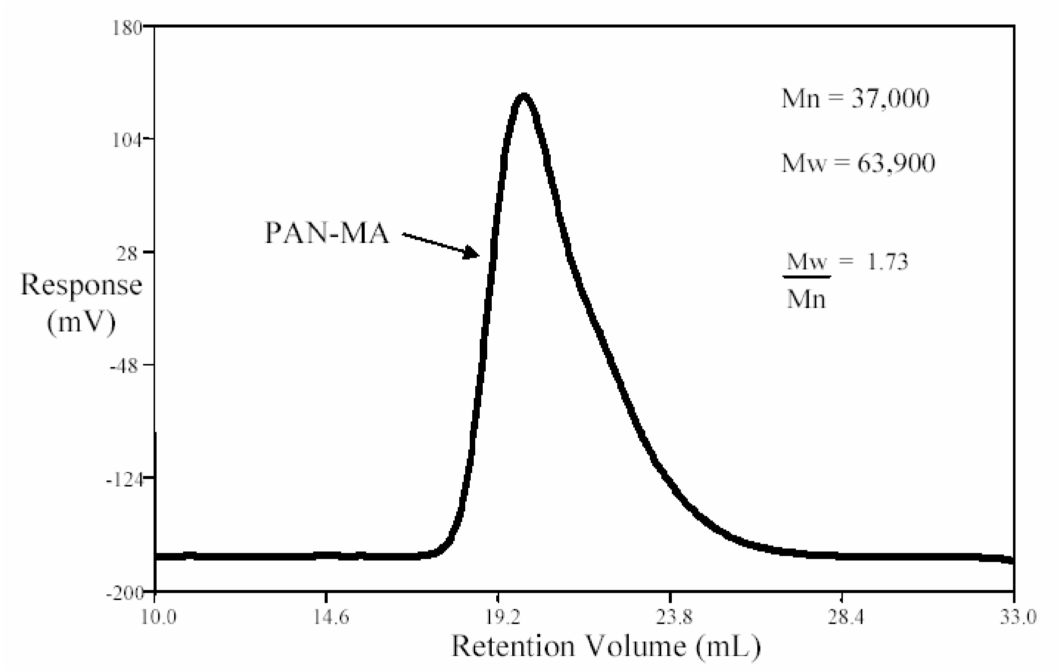
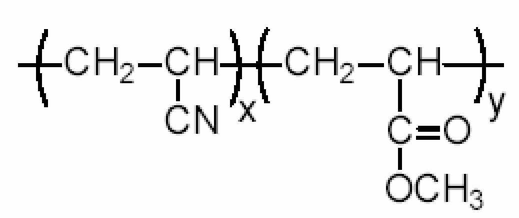


Figure 8: A GPC chromatogram of 85/15 mol% AN/MA copolymer in NMP + 0.02M P_2O_5 at 60 °C (from differential refractive index detector)

The chemical composition of the co- and terpolymers was evaluated using ^1H NMR. Integration of the ^1H NMR signals was used to quantitatively determine the relative amounts of each comonomer present in the final copolymers. Figure 9 shows the ^1H NMR spectrum of an 85/15 AN/MA copolymer and the assigned peaks that were used in the calculations to determine the amount of each comonomer. The integrals of the methyl peak and the methylene peak were used for the calculations to determine the amount of each comonomer that was incorporated into the precipitated copolymer. If x and y represent how many acrylonitrile and methyl acrylate monomer structures were incorporated into the copolymer and the observed values of the integrals for the methyl and methylene peaks are n and m respectively, then the calculations to determine the amount of each monomer incorporated are as follows:



$$\left(-CH_2-\underset{CN}{CH}-\right)_x\left(-CH_2-\underset{\underset{OCH_3}{C=O}}{CH}-\right)_y$$

Three methyl protons give: $3y = n$

Solve for y: $y = n / 3$

Two methylene protons from each structure give: $2x + 2y = m$

Substitute for y and solve for x: $2x + 2n / 3 = m$

$2x = m - 2n / 3$

$x = 1 / 2 (m - 2n / 3)$

Substituting the values for the integrals of each peak into the x and y equations and using the following equation yielded the percent of methyl acrylate that was incorporated into the copolymer:

$$\% MA = \frac{Y}{X + Y} * 100$$

In order to obtain the percentage of acrylonitrile that was incorporated into the copolymer, the percentage of methyl acrylate was subtracted from a value of 100%:

$$\% \text{ AN} = 100\% - \%\text{MA}$$

By using these calculations for the experiment the amount of each comonomer could be determined.[78]

The FTIR spectrum of the terpolymer is shown in Figure 10. The aliphatic C-H stretching is observed at 2931 cm^{-1}, the CN stretching at 2237 cm^{-1}, the ester (of the methyl acrylate) at 1734 cm^{-1}, the keto group (of the benzophenone) at 1666 cm^{-1} and the C-O-C stretching at 1166 cm^{-1}.

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[78] Wiles, K. M.S. Thesis,Virginia Polytechnic Institute and State University. VA, 2002.

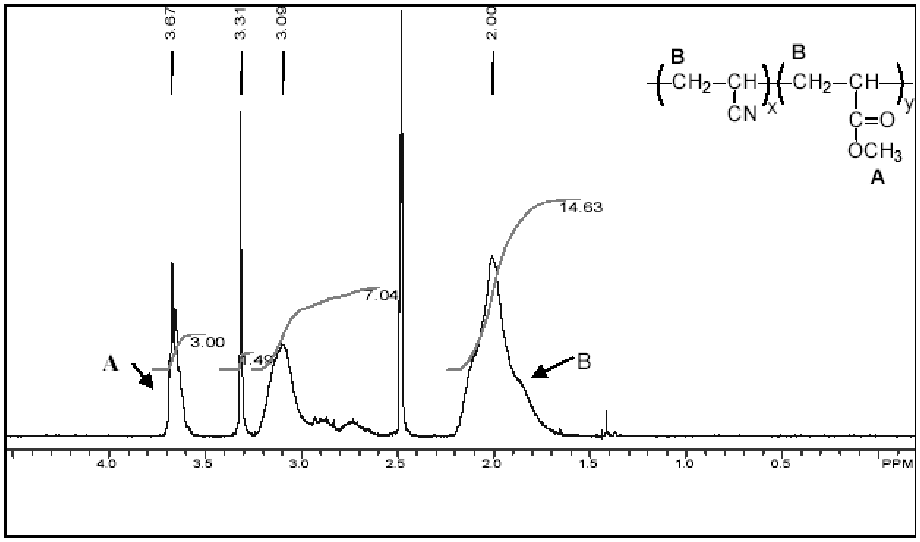

Figure 9: ^{1}H NMR of acrylonitrile and methyl acrylate comonomer peaks in an 85/15 copolymer: A and B peaks correspond to the methyl and methylene groups

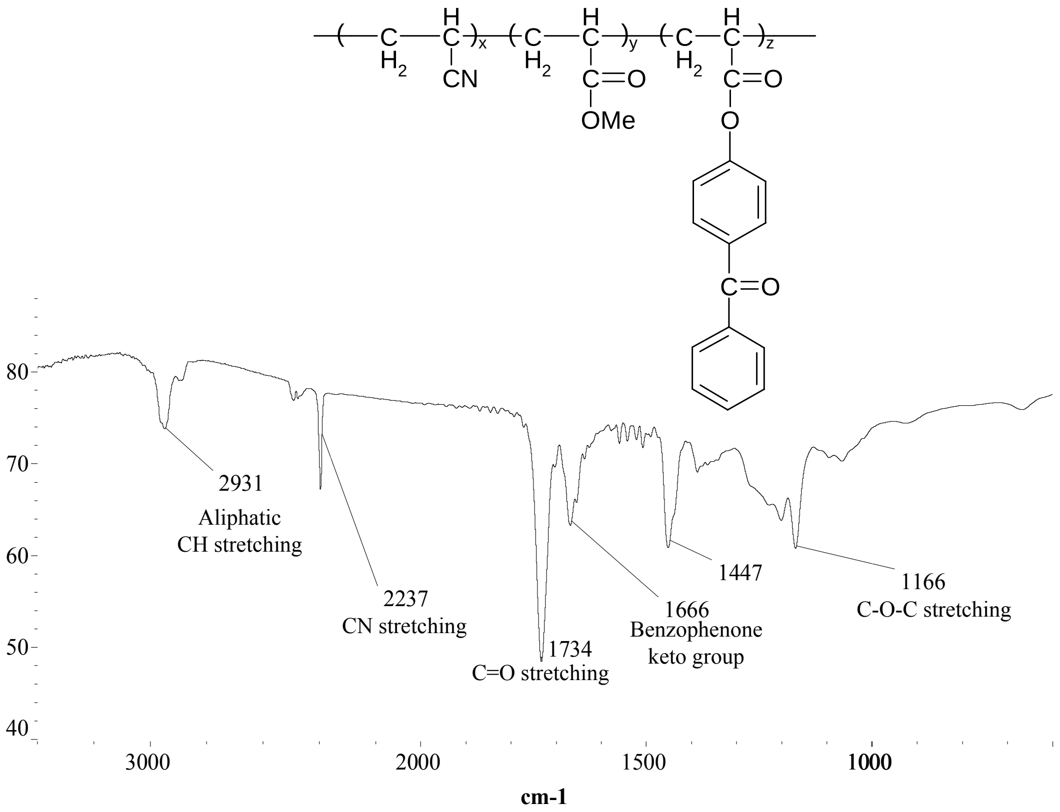

Figure 10: FTIR spectrum of the terpolymer

The terpolymer structure was elucidated by ^1H NMR, which showed that the comonomer mole ratios of the feed were reasonably represented in the terpolymer structure. The spectrum of the 85/14/1 (AN/MA/ABP) terpolymer is given in Figure 11. The aromatic protons appear at δ 7.5 – 8.0, -O-CH_3 at δ 3.7 and –O-CH at δ 3.15 and the –CH_2- around δ 2.0.

Based on the currently developed process, the terpolymer synthesis has been scaled up to kg level by Monomer-Polymer & Dajac Labs, Inc., Feasterville, PA, USA, using the reagents described earlier. The composition and properties of these terpolymers are shown in Table 6. The structure of the terpolymer is given in Figure 12.

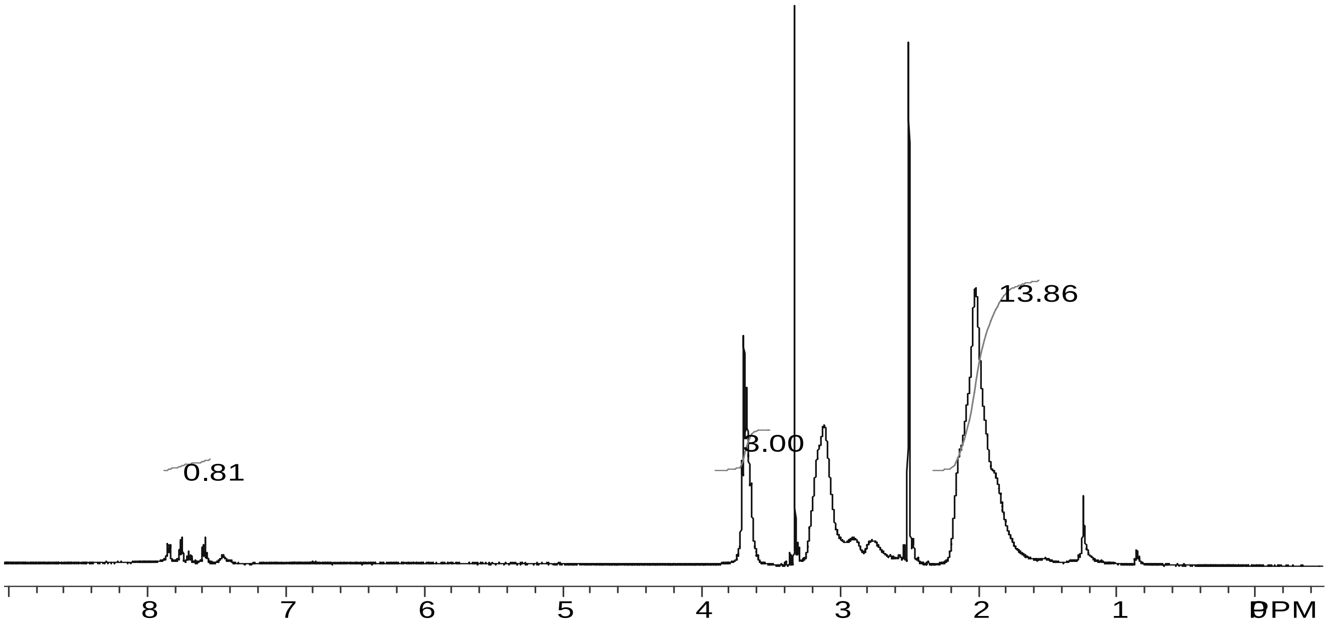

Figure 11: ^{1}H NMR spectrum of the terpolymer

Table 6: Composition and properties of terpolymers

AN/MA/ABP Terpolymer	Monomer Feed	Composition (NMR)	IV* dL/g	Tg ^{0}C	Mn g/mol	Mw g/mol	PDI	Melt Processible
Lab batch	85/14/1	84.3/14.5/1.2	0.50	77	--	--	--	yes
Scale up 1	85/14/1	84.8/13.8/1.4	1.36	91	48000	206000	4.3	no
Scale up 2	85/14/1	84.8/14.2/1.1	0.34	72	16000	36500	2.2	yes
Scale up 3	85/14/1	84.3/14.2/1.4	0.52	76	22000	42000	1.9	yes

* NMP, 25 ^{0}C

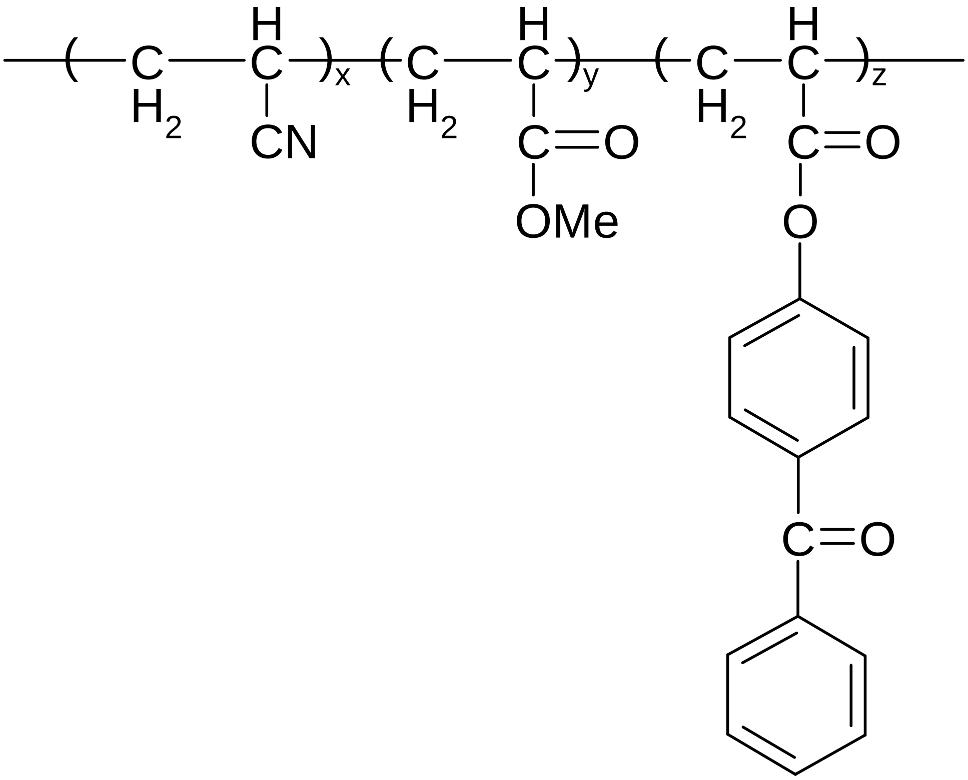

Figure 12: Chemical structure of the terpolymer

Thermal Analysis

Thermal analysis of the terpolymers was carried out to determine the T_gs, the degradation temperatures, and the weight-loss patterns during degradation. The T_gs determined using DSC varied from 77 to 91 °C, depending on the molecular weight. A typical DSC thermogram is shown in Figure 13.

Based on the currently developed process, the terpolymer synthesis has been scaled up to kg level by Monomer-Polymer & Dajac Labs, Inc., Feasterville, PA, USA, using the reagents described earlier. The composition and properties of these terpolymers are shown in Table 6. The structure of the terpolymer is given in Figure 12.

The polymer degradation as measured by DSC appears as a distinct exotherm shown in Figure 14. The initiation of the exotherm is at 322 °C, the peak temperature is at 353 °C and the end temperature is at 380 °C. The heat of degradation was approximately 500 J/g.

The TGA curve of the terpolymer measured in air atmosphere is presented in Figure 15. The curve shows a three-step weight loss and is similar to the weight loss reported for the AN/MA copolymer.[79]

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[79] Guyot A, Bert M, Hamoudi A, Mcneil I, Grassie N. *Eur. Polym. J.* **1978**, *14*, 107.

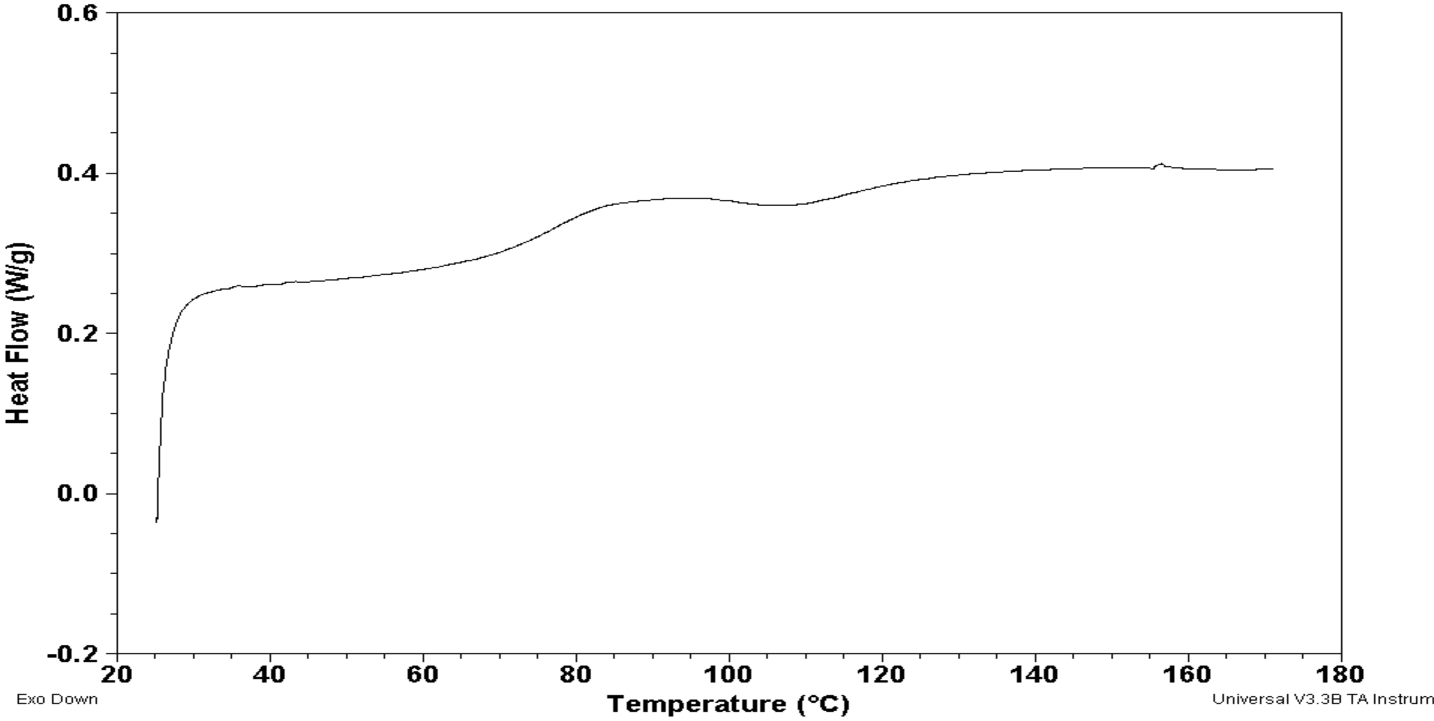

Figure 13: DSC thermogram of the terpolymer, showing the T_g

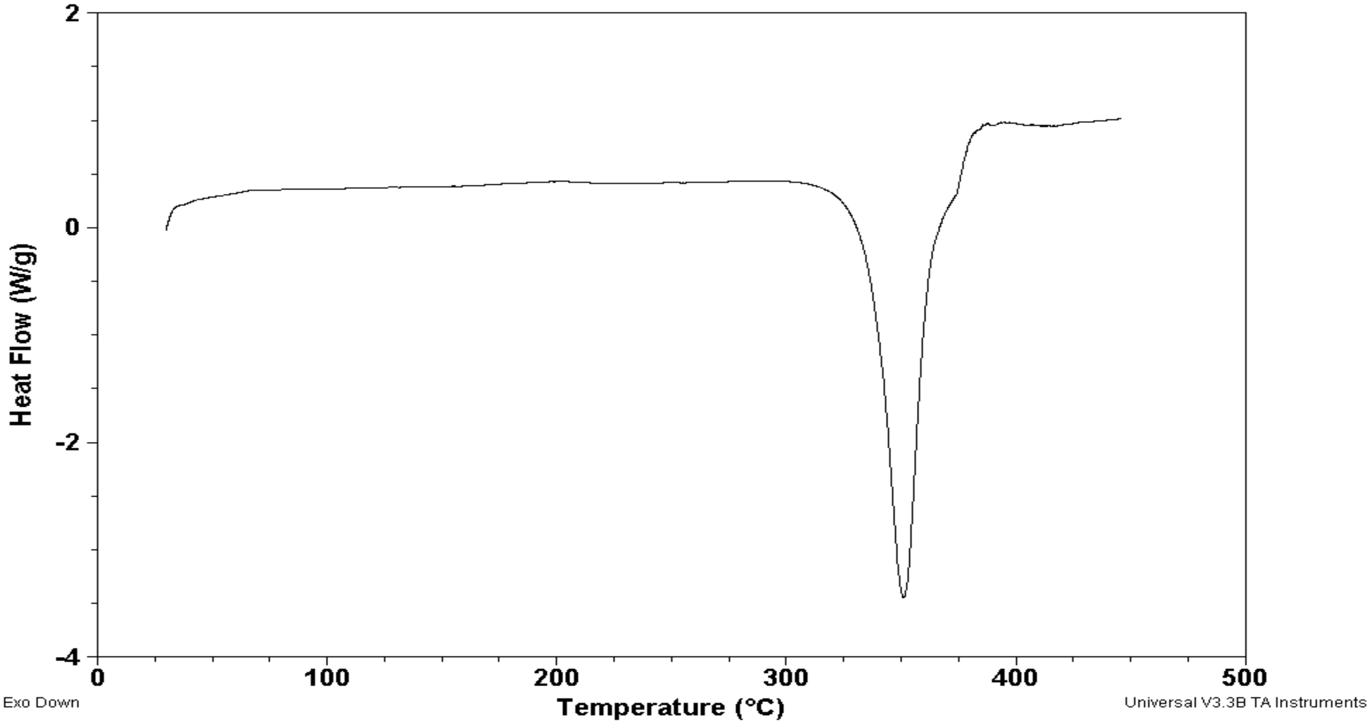

Figure 14: DSC thermogram curve of the terpolymer illustrating degradation

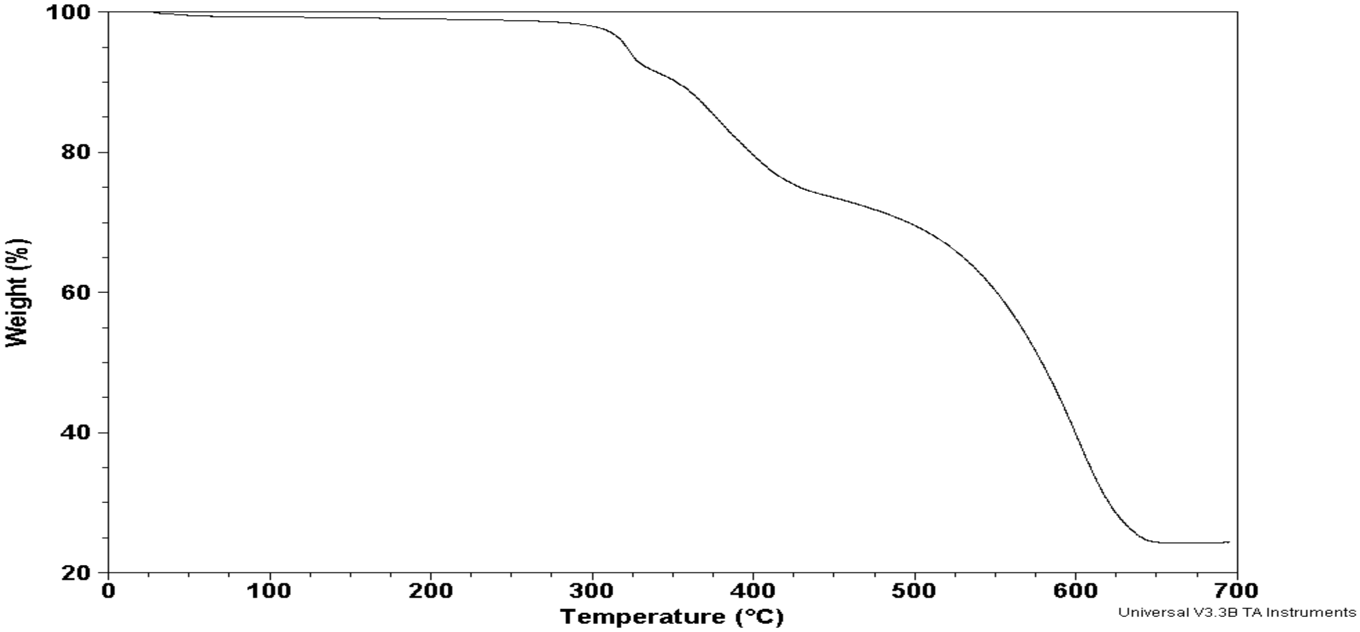

Figure 15: TGA curve of the terpolymer

Melt Viscosity

In the case of AN/MA copolymers, a significant dependence of dynamic melt viscosity on the copolymer composition was observed[80]. Thus, increasing the MA content from 7 to 10 mol% or more caused the melt viscosity to drop by several orders of magnitude. This observation was explained on the basis of a generally accepted view[81, 82] that comonomers like MA can get incorporated in the crystal lattice of AN up to a critical comonomer content and disrupt the characteristic morphology beyond the critical limit.

The copolymer with a 90/10 molar ratio (AN/MA), initially appears to be melt processible but eventually builds up very high viscosity at the melt processing temperature, 220 °C, and is not processible. The 85/15 copolymer, on the other hand, exhibits a steady melt viscosity for about half an hour, during which the fibers could be drawn. This base copolymer composition was, therefore, chosen for the synthesis of the terpolymer. The strategy was to replace about one mole percent of MA with ABP so that the AN content remained the same.[83]

Significance of a Photosensitive Comonomer in the Synthesis of Melt-Processible Precursors

The selection of the photocross-linkable ABP comonomer was guided by the following factors. UV-sensitive monomers are very useful in solvent-free and low volatile-organic-content (VOC) coatings.[84] Several such monomers are used for these applications.[79] The present application requires a comonomer that is incorporated quantitatively and uniformly in the copolymer chain. As discussed above, acrylate monomers as a generic class work well for this

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[80] Bhanu VA, Wiles KB, Bortner M, Glass TE, Godshall D, Baird DG, Wilkes GL, McGrath JE. Polymer Preprints **2002**, *43(2)*, 1017-1018.

[81] Gupta AK, Singhal RP. J Polym Sci Polym Phys Edn **1983**, *21*, 2243.

[82] Groblny J, Sokol M, Turska E. Polymer **1989**, *30*, 1187.

[83] Mukundan T, Bhanu VA, Wiles KB, Bortner M, Baird DG, Wilkes GL, McGrath JE. Polymer Preprints **2003**, *44(2)*, 651-652.

[84] Roffey CG. Photopolymerization of Surface Coatings, Chichester: Wiley; 1982.

purpose relative to other types of monomers. Hence, acryloyl benzophenone (ABP) was selected for the synthesis of the photocross-linkable terpolymer AN/MA/ABP, wherein ABP is used in small amounts (1- 2 mol %). The photochemistry of ABP is well documented.[85] A possible photocross-linking reaction to produce a gelled network may occur in the terpolymer as shown in Figure 16.

A preliminary study of the UV-exposed thin films of the AN/MA/ABP (85/14/1) terpolymer indicated that they began to become insoluble in DMSO after 30 minutes of irradiation and completely insoluble after 2.5 hours of irradiation at room temperature, when exposed to a medium pressure mercury lamp. This suggests that ABP could be effecting the desired cross-linking of the terpolymer. Furthermore, the AN/MA/ABP, 88/10/2 terpolymer has comparable melt stability as the AN/MA (88/12) copolymers and it also has a low enough melt viscosity to be melt processible. Consequently, at least in principle, a photosensitive comonomer may help to make melt processable precursors with ample mechanical strength preceding stabilization.

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[85] Carlini C, Angiolini A. *Adv. Polym. Sci.* **1995**, *123*, 127.

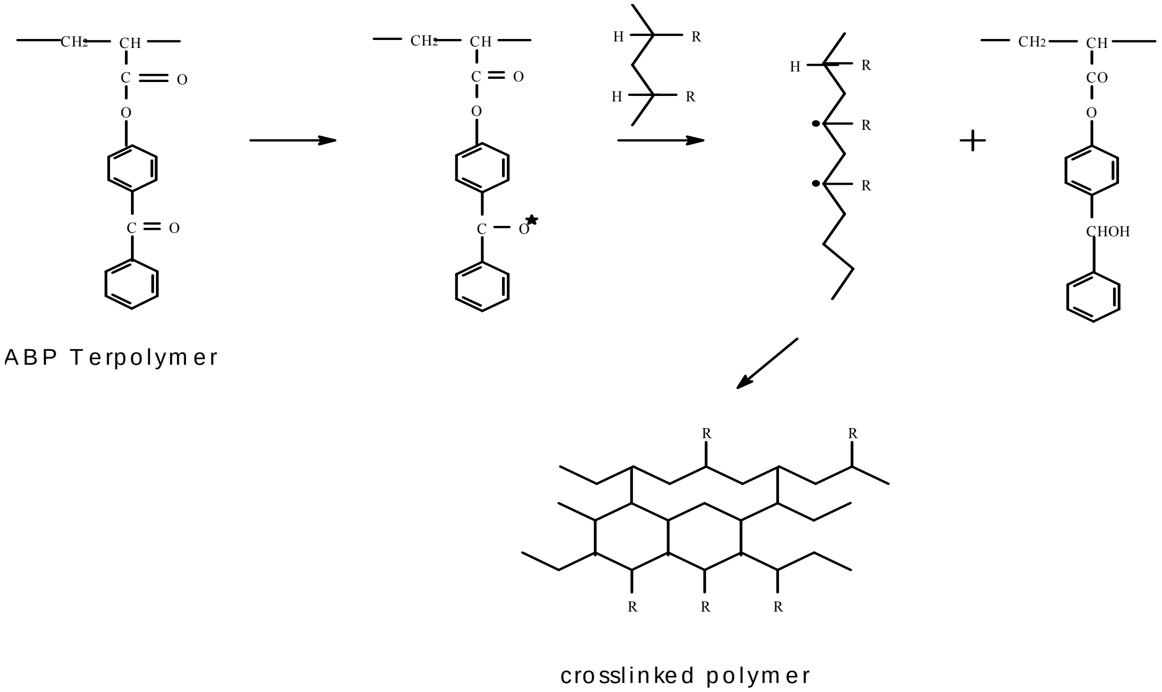

Figure 16: A scheme of the possible photocrosslinking route for the terpolymers

Rheology of Acrylonitrile Copolymers

The steady shear viscosity of the AN copolymers is composition-dependent. The copolymers that contain more than 90 mole percent AN, do not produce a stable melt. Even the composition AN/MA (90/10) does not exhibit a steady shear viscosity for a time that is adequate to spin fibers out of the melt. The steady shear viscosity of the AN copolymers of different compositions are shown in Figure 17. From the figure, it can be seen that AN/MA (85/15) copolymer exhibits a steady melt for about half an hour, which has been empirically found to be long enough to spin fibers from the melt.

The processability window of the 85/14/1 terpolymer is presented in Figure 18. The polymer was treated with boric acid, which stabilized the polymer long enough to produce stable melt viscosity for about 30 minutes.

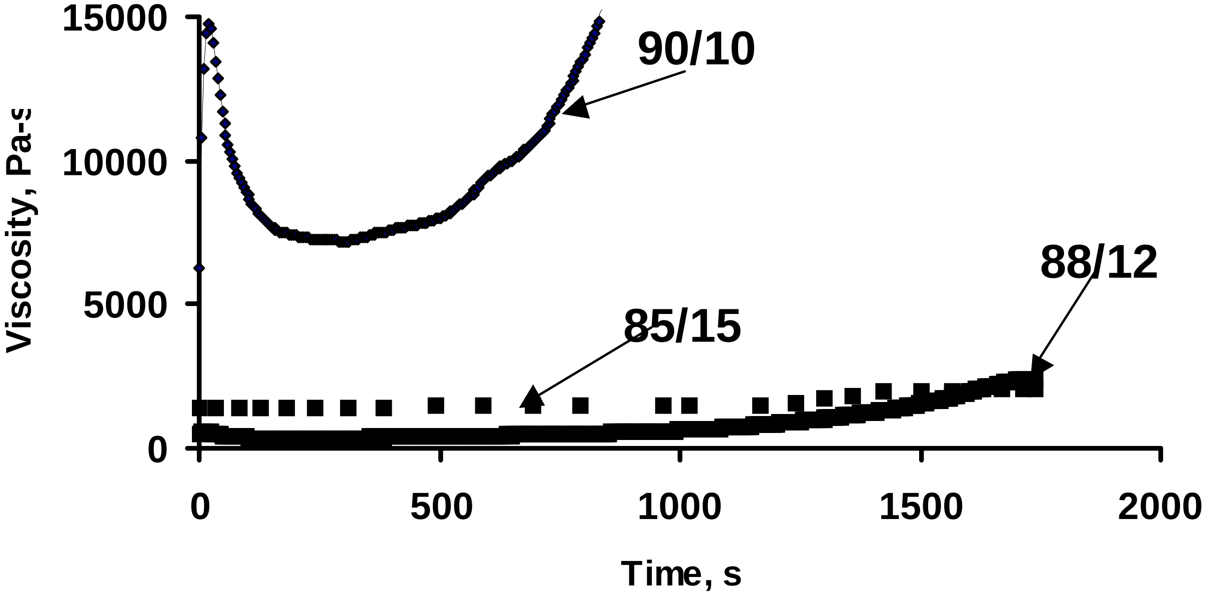

Figure 17: Rheological behavior of the acrylonitrile copolymers, showing that the processing window can be improved by increasing the amount of methyl acrylate comonomer

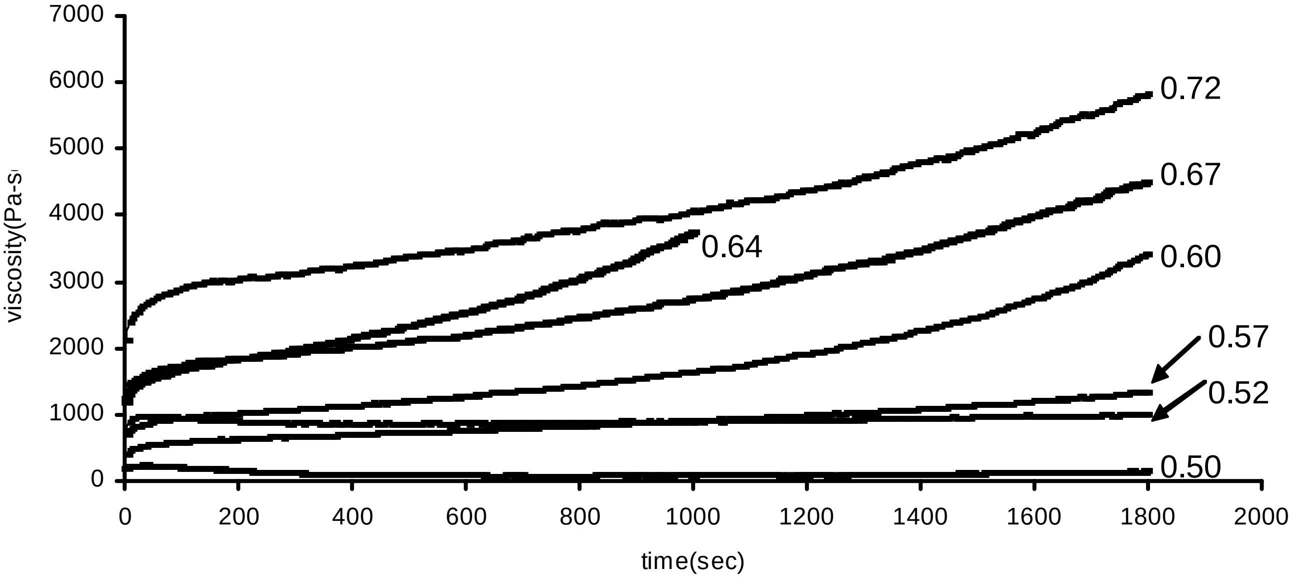

Figure 18: Processability window for the terpolymer is a function of molecular weight

Properties of the Fiber Spun from the Terpolymers

Properties of fibers from terpolymer precursors were tailored by choosing desired melt-processing conditions. Attempts were made to obtain oriented spin-drawn fibers at a maximum winding speed (hence, draw ratio) without breakage in the thread line. For this the winding speed was varied from 100-400 m/min at different throughput rates (0.14 and 0.04 cc/min through the 250 μm capillary) at different spinning temperatures (200 – 210 °C). The present section emphasizes the properties of the spin-drawn fibers at different stages of processing to obtain final carbon fibers. The melt-spinning conditions of the three types of fibers discussed herein are summarized in Table 7. The tensile properties of these fibers at a variety of stages including final carbonized fibers are summarized in Table 8. The tensile stress-strain plots for the as-spun fibers obtained from two types of precursors (intrinsic viscosities 0.34, 0.52 dL/g) are given in Figure 19.

Table 7: As-spun fiber types and their spinning conditions

Fiber types	Precursor IV (dL/g)	Spinning temperature (°C)	Capillary throughput rate (cm^3/min)	Winding speed (m/min)	Draw down ratio
I	0.34	200	0.14	125	40
II	0.52	210	0.14	300	120
III	0.52	200	0.04	275	310

Table 8: Mechanical properties of fibers during different stages

Fiber type	Parameters	As-spun	UV-irradiated	Oxidized	Carbonized
I	No. of specimen tested	15	15	10	11
	Diameter (µm)	40.0 ± 1.7	31.7 ± 1.6	28.8 ± 1.3	23.8 ± 1.4
	Modulus (GPa)	3.35 ± 0.32	4.77 ± 0.41	5.06 ± 0.50	34.9 ±10.4
	Yield strength (MPa)	66.4 ± 6.2	85.5 ± 4.3	--	--
	Tensile strength (MPa)	64.7 ± 7.4	81.5 ± 4.3	101.2 ± 6.9	176.7 ± 75.5
	Strain-to failure (%)	55.9 ± 13.7	2.5 ± 0.3	3.2 ± 1.0	0.47 ± 0.22
II	No. of specimen tested	15	15	14	12
	Diameter (µm)	20.7 ± 0.4	22.7 ± 0.6	17.6 ± 0.6	13.4 ± 0.5
	Modulus (GPa)	5.16 ± 0.32	4.09 ± 0.26	3.94 ± 0.57	52.9 ± 7.7
	Yield strength (MPa)	95.2 ± 5.2	78.8 ± 2.6	--	--
	Tensile strength (MPa)	155.9 ± 6.1	78.8 ± 12.6	119.6 ± 15.3	451.8 ± 162.0
	Strain-to failure (%)	22.2 ± 2.7	13.5 ± 8.2	6.9 ± 1.8	0.90 ± 0.30
III	No. of specimen tested	12	15	15	12
	Diameter (µm)	13.9 ± 0.3	14.2 ± 0.6	14.1 ± 3.1	7.3 ± 0.7
	Modulus (GPa)	6.85 ± 0.35	5.10 ± 0.89	6.02 ± 1.2	126.0 ± 15.6
	Yield strength (MPa)	111.5 ± 6.3	91.8 ± 12.2	--	--
	Tensile strength (MPa)	234.8 ± 10.7	116 ± 20.5	159.5 ± 30.2	594.1 ± 147.5
	Strain-to failure (%)	14.6 ± 0.9	16.5 ± 4.4	7.5 ± 2.1	0.42 ± 0.11

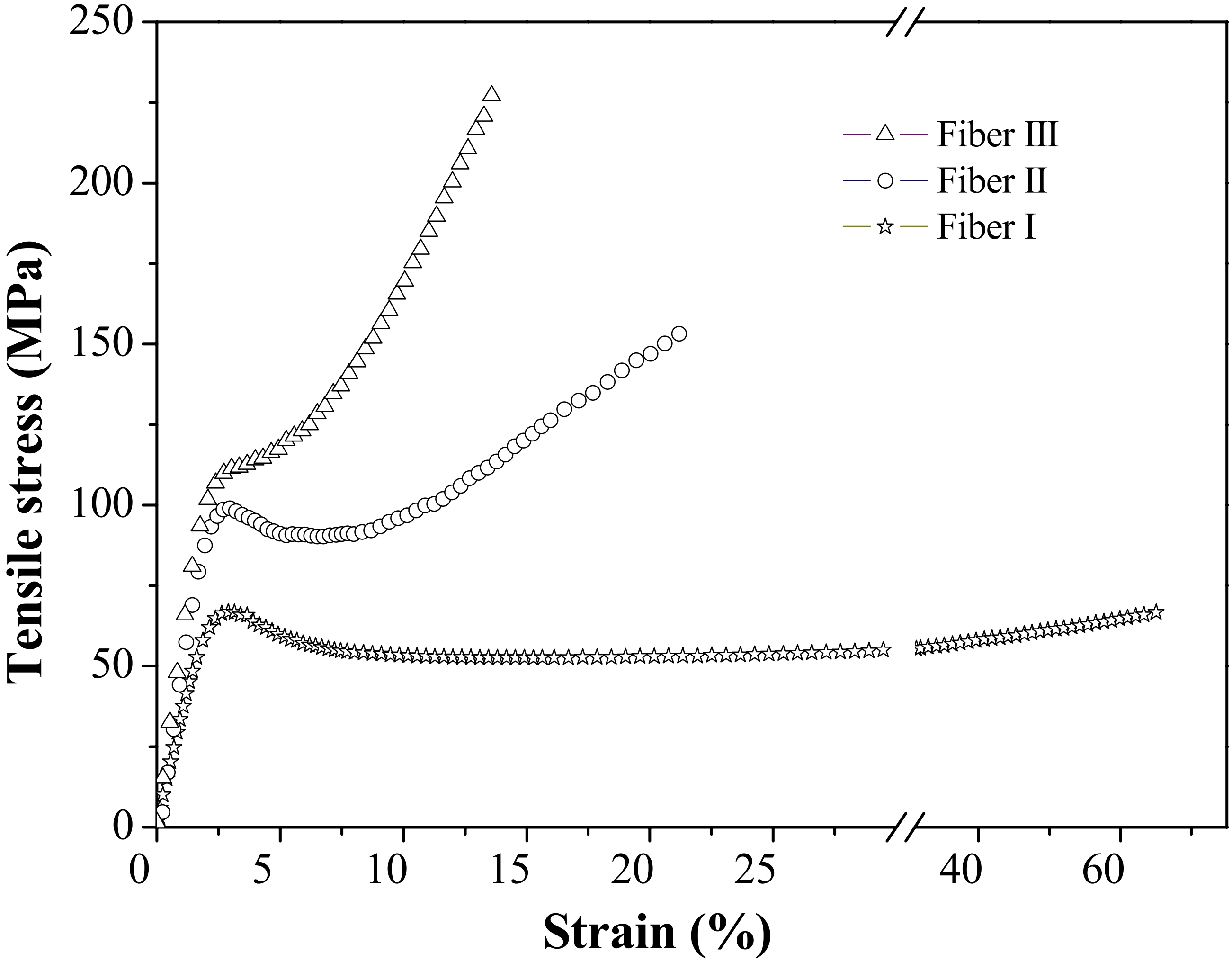

Figure 19: Stress-strain curves of as-spun fibers.

The copolymer with an IV of 0.34 dL/g could be drawn down only to 40 at 200 °C, and consequently it displays a very high strain-to-failure of about 60 % and a low tensile strength of roughly 65 MPa. The high molecular weight precursor drawn down to 120 and 310 to get as-spun fibers have approximately 21 and about 14 μm, respectively. Increase in draw ratio caused increased modulus, yield and tensile strengths with lowering in ultimate elongation.

The fibers were successfully stabilized by UV irradiation at 110 °C. It was observed that the stabilization of highly oriented fibers at temperatures higher than 110 °C was complicated due to high shrinkage force, which caused fiber breakage during radiation processing and succeeding oxidative stabilization steps. Figures 20 and 21 display the tensile stress-strain plots for the UV-irradiated and oxidatively stabilized fibers, respectively.

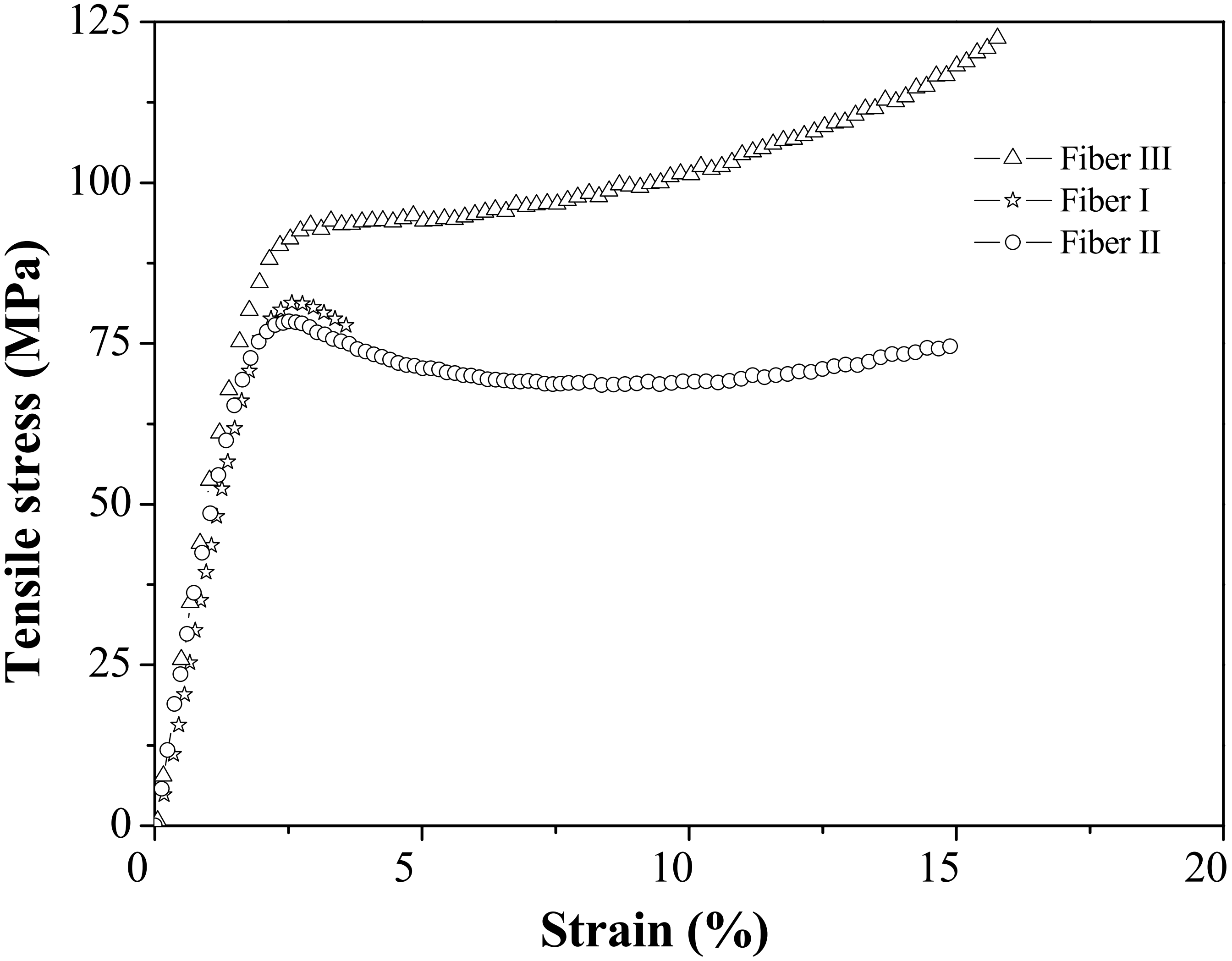

Figure 20: Stress-strain curves of UV irradiated fibers

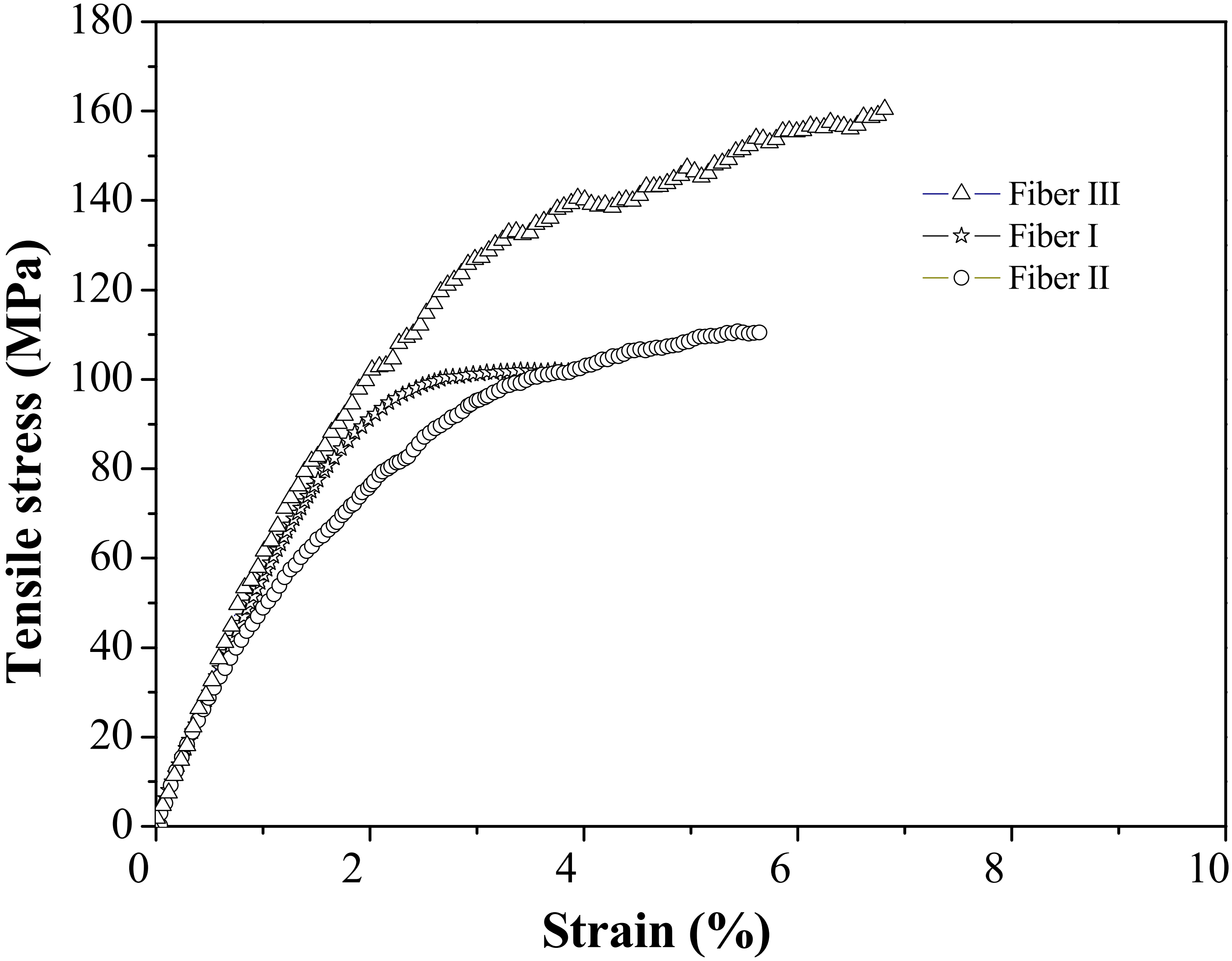

Figure 21: Stress-strain curves of oxidized fibers

Fiber I shows very low strain-to-failure and slightly lower modulus than the others. However, the tensile strengths and yield strengths for fibers I and II after irradiation are analogous. Table 9 shows that after UV irradiation, the tensile strength of fiber I was slightly improved but the strengths for the others were lowered. Possibly, because of lower molecular weight and high segmental mobility during the UV processing, fiber I became efficiently crosslinked, which improved the load sharing among chains. The highly oriented fiber III displayed better properties than the others. Similarly, after the oxidative stabilization, fiber III displayed better properties; fiber I showed the least strain-to-failure but higher modulus than II, as that was crosslinked efficiently as given in Figure 20 and Table 8. UV crosslinking not only prevents fiber breakage due to melting during oxidative stabilization but also retards relaxation of fiber through loss in orientation.

The stress-strain plots for the carbonized fibers are displayed in Figure 22. It can be seen from Figure 22 and Table 8 that the tensile strength and modulus increased relative to draw ratio of the as-spun fibers. Carbonized fiber I, being of low molecular weight and low draw ratio, shows a modulus of about 35 GPa, while those of fibers II and III are approximately 55 and 130 GPa, respectively. Retention of fiber orientation with minimum relaxation during stabilization is desired. A high dosage irradiation process for faster stabilization is under development for the highly drawn fibers.

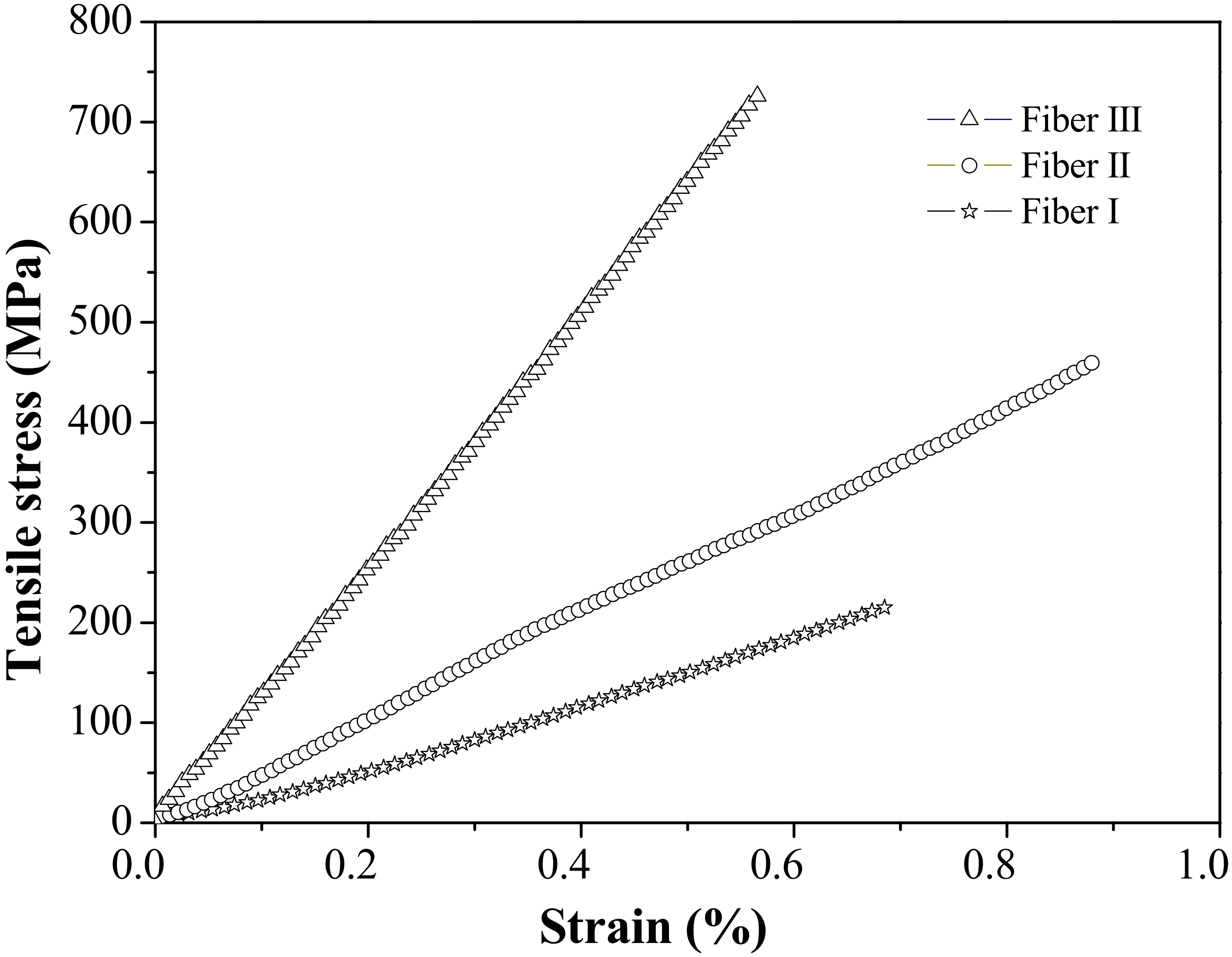

Figure 22: Stress-strain curves of carbonized fibers

At different stages of processing, (i.e., as-spun, UV crosslinked, oxidatively stabilized and carbonized) fiber III exhibits various mechanical strengths and weaknesses. As-spun fibers show ductility (fibriller failure pattern), which progressively disappears by crosslinking and cyclization in the successive steps and the failure pattern becomes brittle (catastrophic failure). The cross-section of failed carbon fibers (Fig. 24 D) shows defects inside the fiber. The lateral surface of the carbonized fiber was found to be very smooth (Fig. 24 A). However, failed carbon fibers show pits and scales on the surface (Fig. 24 B). The presence of surface defects also causes fiber failure. Although the moduli of the carbonized fibers were very good, gross defects in the fiber caused failure at a lower strain level (~0.5 %) resulting in poor tensile strength of the carbonized fiber relative to the commercial fibers. Carbonized fiber III displayed a tensile strength up to ~730 MPa, with a modulus up to ~140 GPa, whereas that of the commercially available fibers are in the range of ~2 GPa, and ~200 GPa, respectively. The mechanical strength of the carbonized fiber is given in Figure 23. The mechanical strength of carbon fiber can be influenced by defects in the fibers themselves. An SEM micrograph shows these defects (Fig. 24).

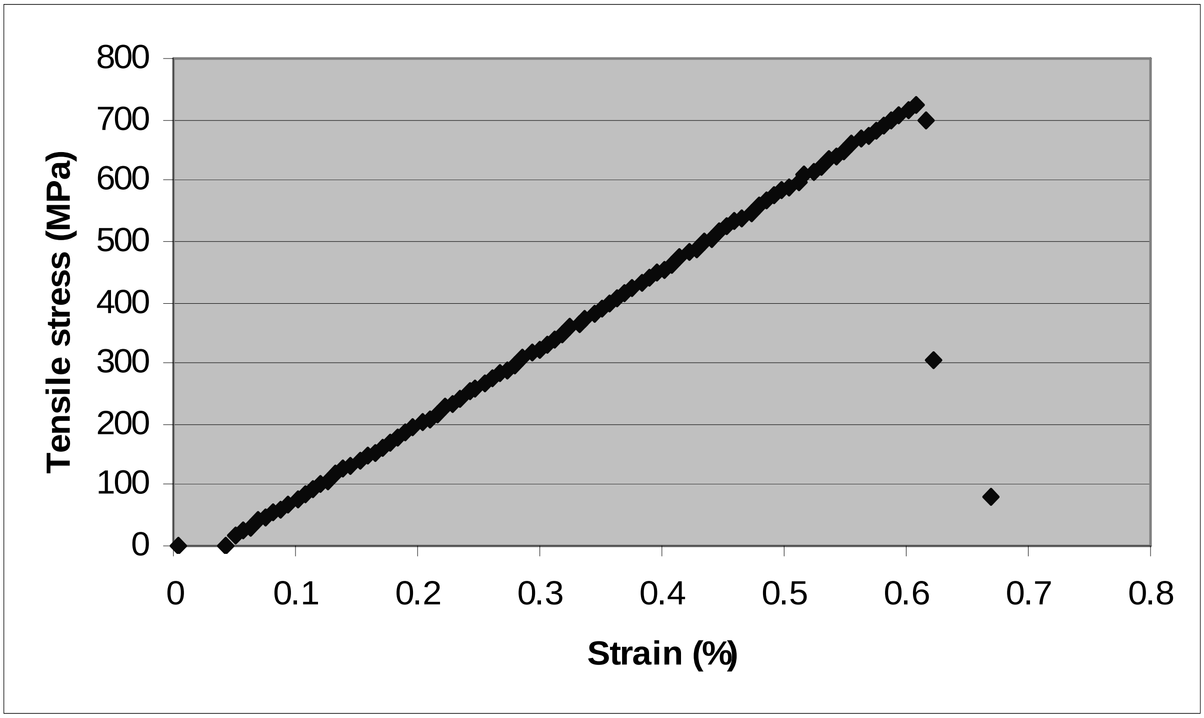

Figure 23: The mechanical strength of carbonized fiber III.

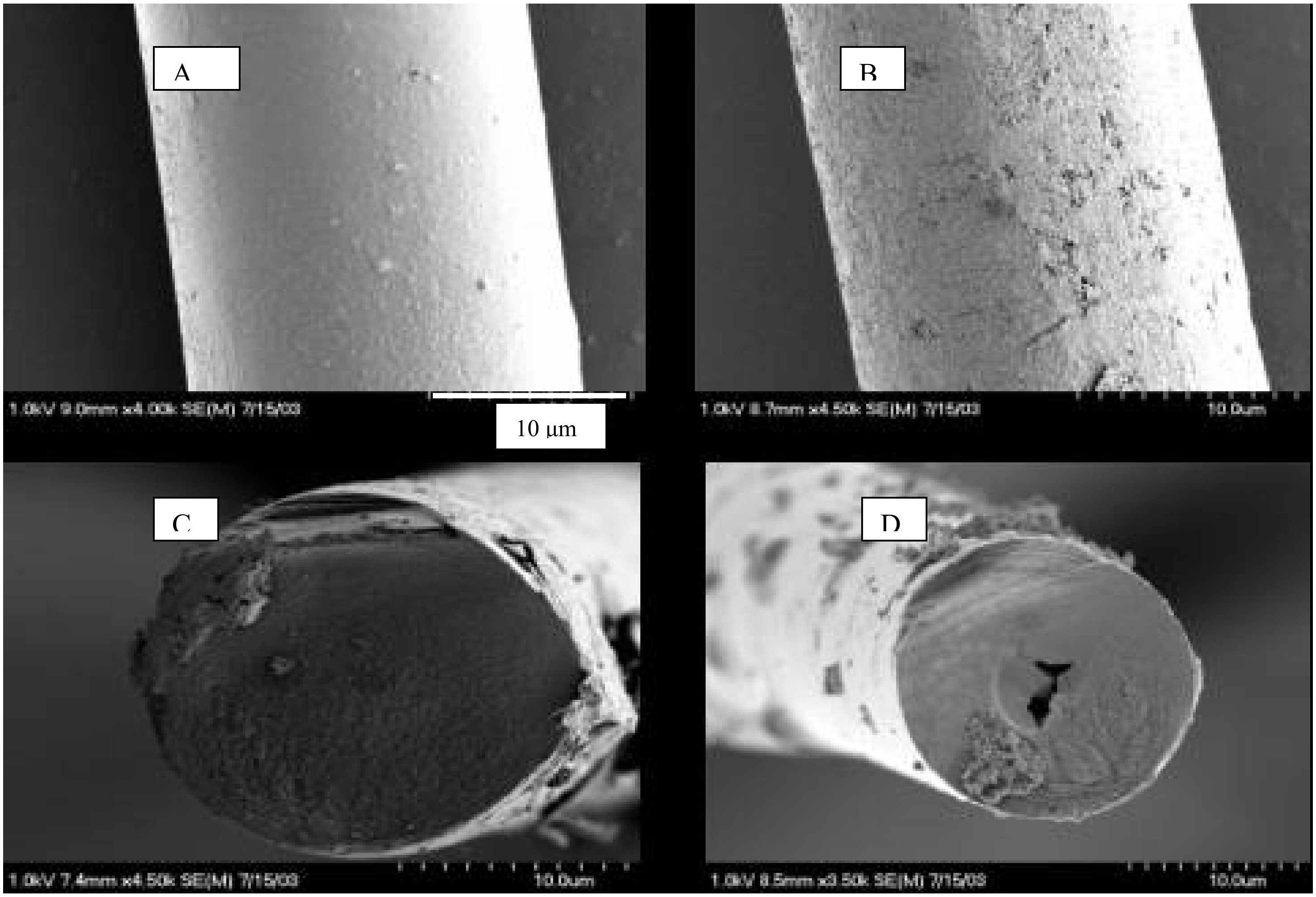

Figure 24: A SEM micrograph of unflawed (A,C) and flawed fibers (B,D)

Synthetic Variables Affecting Copolymer Behavior

There have been difficulties in finding the right combination of comonomer ratios for a suitable AN/MA copolymer that is melt processible. The next component of this dilemma is how to design a system that could solve these problems. The comonomer ratio was AN/MA 88/12 and the synthetic variables that may lead to the understanding as to how best to improve this problem were CTA, initiator, and surfactant. For each of the three variables there was a variation of concentration ranging from low to high to determine a method of getting the desired molecular weight with these synthetic variables. However, there are many criteria that can affect the consistency of molecular weight design. This thesis included an initial attempt to confront this daunting task.

The concentration flow chart corresponds to the different concentrations of CTA and the series of samples 1A through 3. For this tier there were four syntheses preformed. The second tier, 1B- 3, corresponds to the different initiator concentrations ranging from very low to high. The final tier is the same as the previous two except the variable is surfactant concentration. The letters (A,B,C) correspond to CTA, initiator, and surfactant for organizational purposes.

Table 9 shows that the molecular weight and the intrinsic viscosities show similar trends. The CTA opens a window into understanding how these molecular weights have decreased with increasing mol% CTA. Increasing the CTA causes the molecular weight and I.V. to decrease, which correlates to literature results. The effect of initiator on molecular weight and I.V. is given in Table 10. These trends also agree with literature results. As the mol% of the initiator increases, the I.V. and molecular weight decrease.

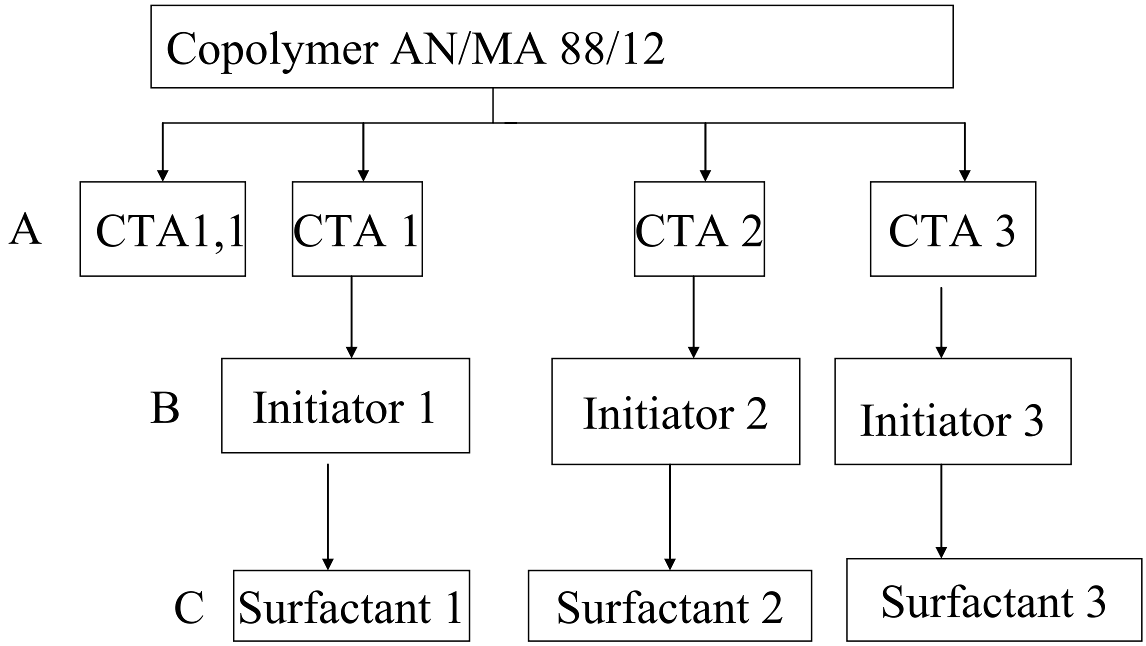

Figure 25: Concentration flow chart of synthetic variables. A denotes chain transfer agent, B denotes initiator, and C denotes surfactant. For A, B, and C, concentration increases from left to right

Table 9: The effects of CTA concentration on copolymer molecular weight and I.V.

Chain Transfer Agent (CTA) Samples 1A	Mole % CTA	Intrinsic Viscosity (I.V.) [η] dL/g NMP@25 ^{0}C	GPC M_W NMP@25 ºC
1, 1	0.5	1.65	310,000
1	1	0.56	106,000
2	2	0.31	49,600
3	4	0.24	33,600

Table 10: Initiator effect on molecular weight and I.V.

Initiator Samples 1B	Mole % Initiator	Intrinsic Viscosity (I.V.) [η] dL/g NMP@25 ºC	GPC MW NMP@25 ºC
1	0.008	0.46	50,940
2	0.016	0.39	44,984
3	0.033	0.30	29,987

The last tier exhibits its own set of unique circumstances, some of which will be discussed. The surfactant concentration proved to be the most difficult variable in designing a clear-cut way to use a surfactant as a means to control molecular weight. The surfactant is difficult to remove from the sample. Table 11 shows the effect that the different surfactant concentrations have on the copolymer.

Table 11: Surfactant (Dow-Fax) effect on the I.V. and molecular weight

Surfactant Samples 1C	Mole % Surfactant	Intrinsic Viscosity (I.V.) [η] dL/g NMP@25 C	Intrinsic Viscosity (GPC) [η] dL/g NMP@25 C	GPC MW NMP
1	0.395	0.33	0.36	26,051
2	0.79	0.40	0.39	33,556
3	1.58	0.34	0.38	45,640

Chapter V: Conclusions

Terpolymeric melt processible carbon fiber precursors have been synthesized and characterized by IR, NMR, GPC, intrinsic viscosity and rheological tests. A general correlation between the melt viscosity and copolymer composition was observed. This study also showed that the design of melt processible copolymer precursors needs to be based on criteria such as reactivity ratios, T_g, melt viscosity and melt stability as a function of time. In addition, the thermal behavior of the copolymers must also be qualitatively similar to conventional polyacrylonitrile precursors. Acrylates in general, and MA in particular, are the most suitable comonomers to synthesize AN-based melt processible precursors for carbon fibers. The addition of photosensitive comonomers like ABP is desirable for photocrosslinking the fiber or film and to make precursors that will have enough mechanical strength to resist fusing during the stabilization step. The most suitable composition of the precursor appears to be AN/MA/ABP in the molar ratio of 85/14/1.

Chapter VI: Suggested Future Research

The study reported in this thesis involving PAN precursors for carbon fibers could be furthered refined by performing a more detailed study on the effects of boric acid on enhancing melt stability. More research on the effect of particle size on the melt stability would also be useful. Since the surfactant has a marginal effect on the intrinsic viscosity, perhaps a study on how the surfactant and other sulfate-containing compounds used in polymer synthesis could enhance the desired molecular weights for melt processing would be interesting. Furthermore, use of lower concentrations of $MgSO_4$ for precipitation could possibly reduce the effect that is imposed by residual compounds. There could be continued research on the addition rate of the monomers and how they can influence the desired molecular weight and the molecular weight distribution. Completing a series of different molar ratios under the same conditions to determine if the research thus far will continue to be consistent with different molar concentrations (85/15, 88/11/1, 85/14/1). A study on the temperature at which the co- and terpolymers were precipitated and the influence that these various temperatures would have on the resulting polymers molecular weight and the molecular weight distribution would also be interesting. Continued studies on investigating the properties of carbonized fibers from this novel melt processible precursor would be another possible avenue.

Vita

Harry D. Johnson, son of Mr. and Mrs. Harry and Hattie Johnson was born in Fresno, California. He was raised in San Francisco, California where he attended primary and secondary school. The schools that he attended were John Mclaren and Ulloa elementary, Luther Burbank, James Lick Junior High located in San Francisco. Harry attended Balboa High School where he was a scholar athlete, after graduating he went to West Hills Junior College where he continued his athletic career. He received several offers to attend several (Division I) schools such as, University of Oregon, University of Washington, Florida State University, University of Utah etc. Harry selected Grambling State University where he excelled academically and athletically. Harry chose to leave school to pursue a professional athletic career upon completing that segment of his career he returned to Grambling State University where he completed dual degrees in biology and chemistry. After graduating from Grambling State University Harry entered the Macromolecular Science and Engineering program at Virginia Polytechnic Institute and State University under the guidance of Professor James E. McGrath, during which time he presented posters at a national conference of the American Chemical Society. He obtained his Masters in Macromolecular Science and Engineering, in 2006. His immediate plans are to seek employment or continue his education.