

Nanofibers and spheres by polymerization of cyanoacrylate monomer

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Abstract

A unique method for creating polymer nanofibers and spheres on a variety of substrates is described. Cyanoacrylate monomer vapor was collected on a solid surface and polymerized to form nanofibers. Tiny spots of initiator on the surface of a substrate and small monomer droplets in a monomer vapor appear to be required for the growth of the polycyanoacrylate nanofibers. The polycyanoacrylate nanofibers create a network and increase the specific surface area significantly.

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1. Introduction

In filtration applications, the smaller the diameter of the fiber, the higher the capture efficiency per unit mass of fiber [1,2]. Very thin fibers made by processes such as electrospinning [3] are widely used for filtration. In this work, many thin fibers attached to and growing within a mat of larger fibers decreased the size of pores between the larger fibers [4]. Modification of existing surfaces and pore structures can enhance and be useful in filtration, catalysis, adsorption, and textiles.

Polymerization of cyanoacrylate vapor is used in forensic science for development of latent fingerprints [5] and for replication of ice crystals [6]. Nanofibers were created when droplets of cyanoacrylate monomer vapor were collected on electrospun nanofibers that had minute quantities of water on the surface of the fiber [7]. During our initial experiments on the polymerization of droplets collected from cyanoacrylate vapor, which were aimed at creating permanent attachment between nanofibers, polycyanoacrylate spheres were created. Subsequent experiments showed that polycyanoacrylate (PCA) nanofibers were also formed under reproducible conditions on

a variety of substrates. Some of these PCA nanofibers were straight for distances of several microns while others were tapered, rough or bent.

2. Experiments

Cyanoacrylate monomer was heated in air at a controlled temperature, which caused steady evaporation and formation of a vapor of airborne droplets. These droplets were captured on various substrates. The list of substrates include: poly(*meta*-phenylene isophthalamide), also known as Nomex[®] or MPD-I; nanofibers made by electrospinning [8]; MPD-I microfibers; glass microscope slides; and thick fibers of polypropylene in a woven mesh. Weak bases are known to initiate polymerization of cyanoacrylate. Water, when present on the substrate, initiated the anionic polymerization [7]. Fig. 1(a) is a schematic diagram of the experimental setup used. The temperature of the hot plate was controlled by a digital temperature controller (Omron E5EN) and measured with a thermocouple (K type, 0.8 mm wire) below the vial, which contained a few milligrams of liquid monomer. The amount of liquid monomer, denoted as CA is exaggerated in Fig. 1(a). The vial was placed inside a bottomless conical-shaped glass vessel. A circular washer (Fig. 1(b)) was placed in the top section of the glass vessel. The temperature at the position where washer was placed was 40 °C when the temperature below the vial was 108 °C. The conical glass vessel was closed at the top with a glass closure. The morphology (fibers or spheres) was varied by changing the temperature of monomer vaporization in the range from 100 to 180 °C. The length of fiber was controlled by varying the

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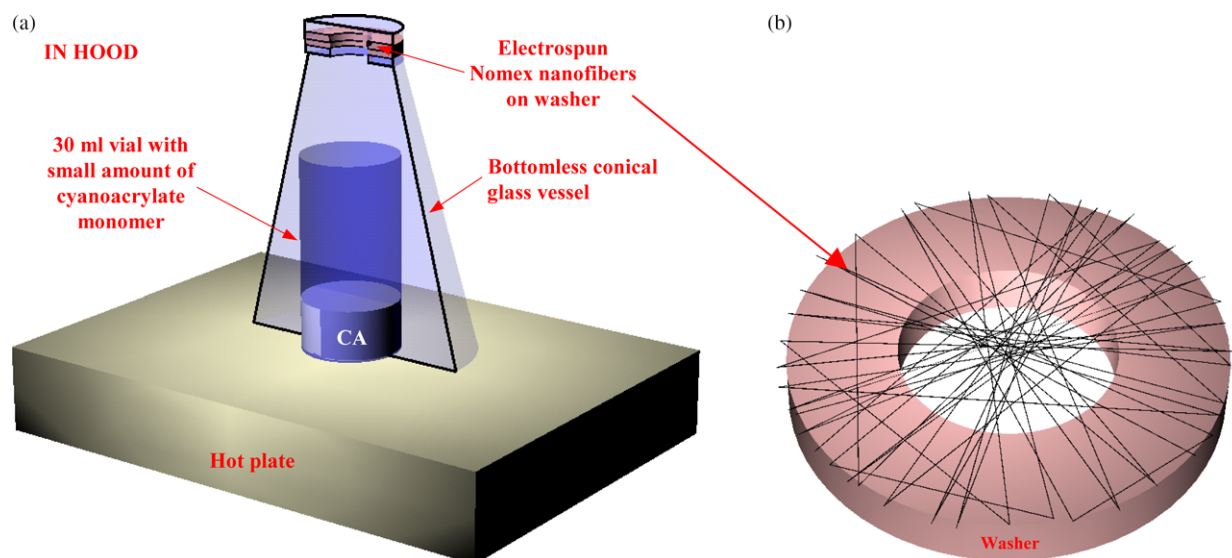


Fig. 1. Schematic drawing of the experimental setup used (a) and enlarged image of electrospun nanofibers supported on a washer (b).

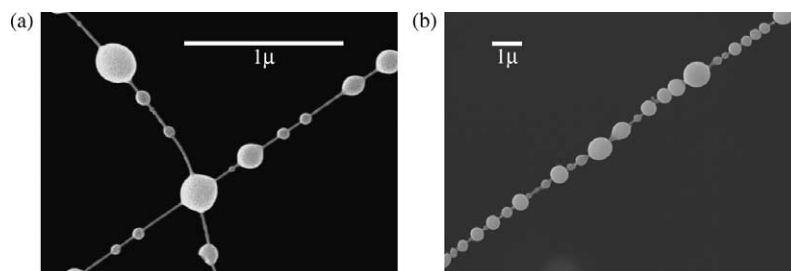


Fig. 2. Scanning electron micrographs of PCA beads on nanofibers, (a) at a crossing point, and (b) at many points along the fiber.

exposure time of the substrate to the vapor in the range from 15 min to 12 h. To investigate the polymer initiation, the substrate was exposed to water vapor and then to monomer vapor. The results obtained were compared with a similar substrate that was not exposed to water vapor. The polymerized structures were observed with scanning electron microscopy and transmission electron microscopy.

3. Results and discussion

The cyanoacrylate vapor was collected as small spherical drops on electrospun nanofibers. The drops grew larger as more cyanoacrylate droplets were collected from the vapor. The drops often polymerized into solid spherical beads on the fibers. Some droplets, at points where two electrospun nanofibers crossed, polymerized and formed mechanical connections between the crossed fibers (Fig. 2(a)).

Fig. 3 shows PCA nanofiber branches that formed on MPD-I fibers. Cyanoacrylate vapor polymerized to produce the nanofiber branches. The polymerization occurred more rapidly on the tip than elsewhere. This indicates that the initiator was carried on the tip of the growing nanofiber. The temperature at which the monomer was vaporized affected the size of the droplets in the vapor, which in turn affected the morphology of the PCA structures that formed. At lower monomer vaporization

temperatures ($\geq 100\text{ }^{\circ}\text{C}$) PCA fibers were formed while at higher monomer vaporization temperatures ($\geq 180\text{ }^{\circ}\text{C}$) PCA spheres were formed. The length of the polymerized nanofibers increased as the time of exposure to the vapor increased (Fig. 4).

Pre-exposure of the substrate to moist air increased the number of PCA fibers per unit area (Fig. 5(a) and (b)). Drying the substrate by heating decreased the number of fibers per unit area. The number of PCA fibers was varied by increasing or decreasing the exposure of the substrate to water vapor.

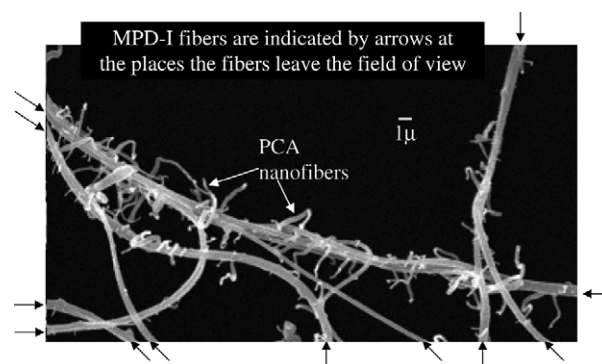


Fig. 3. Scanning electron micrograph of PCA nanofibers obtained by exposing long MPD-I nanofibers to small droplets of cyanoacrylate vapor, which was vaporized at $134\text{ }^{\circ}\text{C}$.

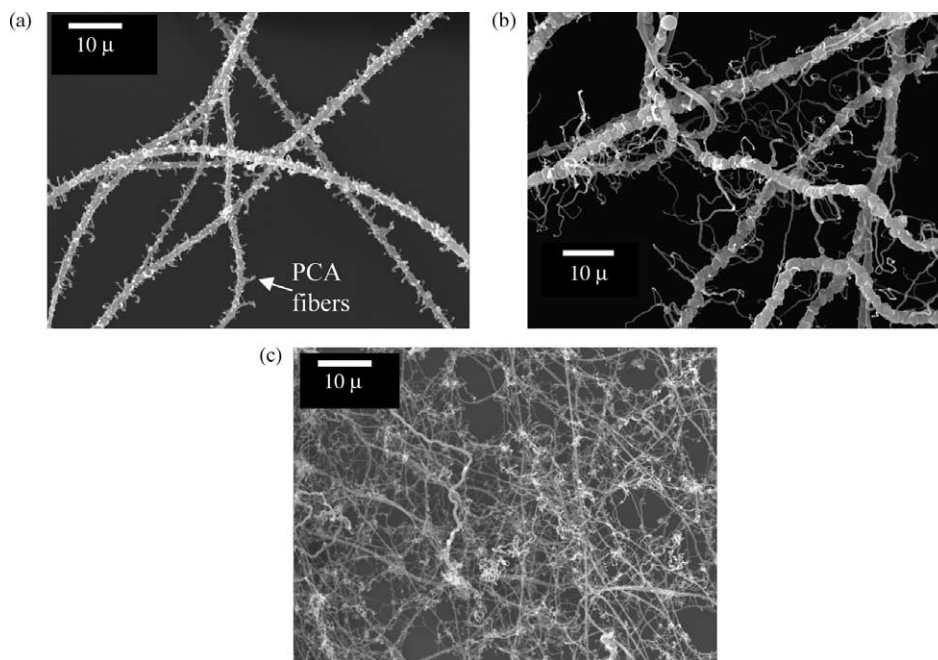


Fig. 4. Scanning electron micrograph of PCA nanofibers obtained by exposing long MPD-I nanofibers to cyanoacrylate vapor for times of 15 min (a), 30 min (b), 12 h (c) respectively, all at 160 °C. In all the samples same amount of cyanoacrylate monomer (50 mg) was used.

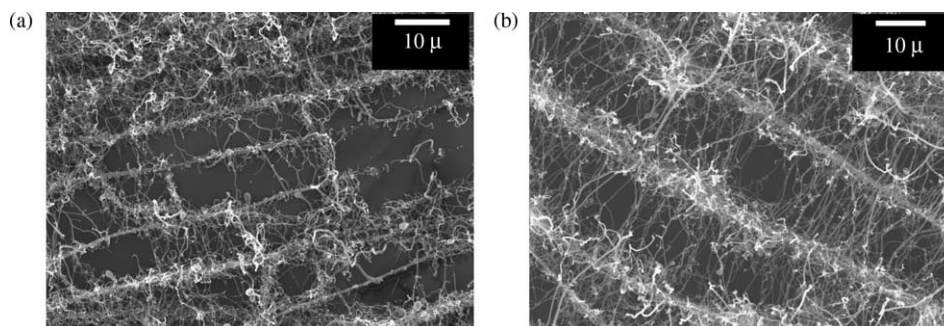


Fig. 5. (a) Scanning electron micrograph of PCA nanofibers obtained by exposing long MPD-I nanofibers to cyanoacrylate vapor. (b) More PCA fibers per unit area grew on MPD-I fibers when the MPD-I fibers were exposed to water vapor and then exposed to cyanoacrylate vapor. In both samples the same amount (50 mg) of cyanoacrylate monomer was vaporized at 160 °C and the exposure time was 1 h.

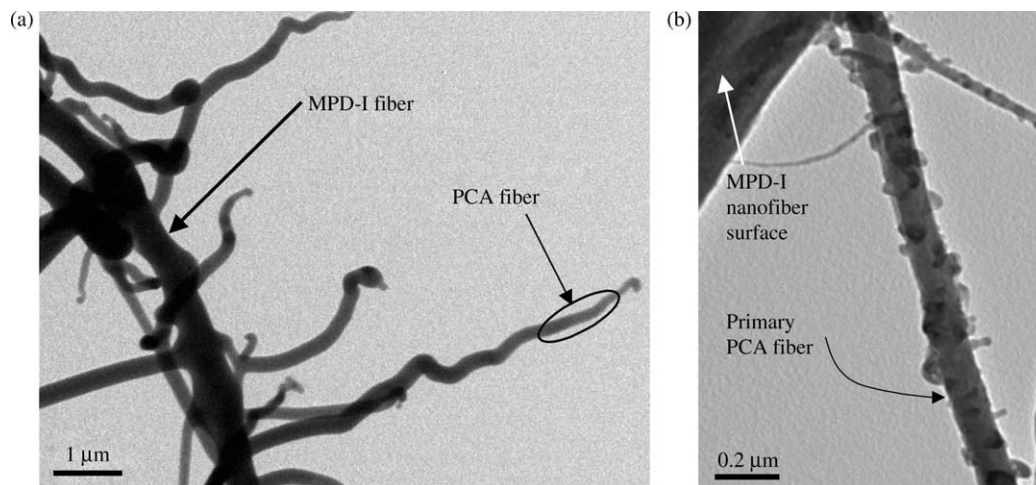


Fig. 6. (a) Transmission electron micrograph showing smooth PCA nanofibers on a MPD-I fiber. (b) Transmission electron micrograph of PCA fibers with secondary PCA branches formed due to presence of water vapor during the growth of PCA fibers.

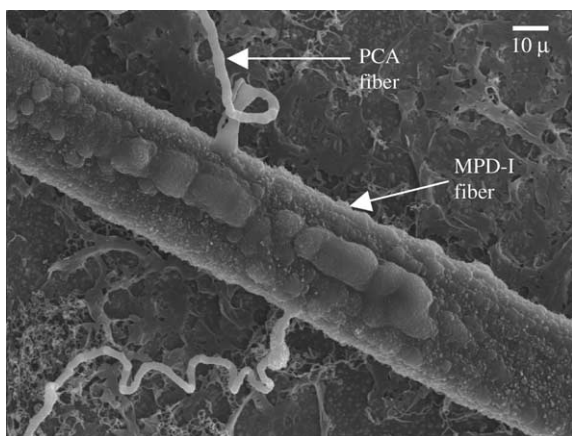


Fig. 7. Scanning electron micrographs of PCA fibers observed on a large diameter MPD-I microfiber after exposure to cyanoacrylate vapor. Irregular structures of PCA that grew on the background glass substrate are shown.

When water vapor was introduced during the growth of primary PCA fibers, smaller fibers and particles grew on the primary PCA fibers, but not on the MPD-I nanofiber (Fig. 6(b)), perhaps because PCA is more hydrophilic than MPD-I.

Larger diameter PCA fibers grew on MPD-I microfiber (Fig. 7) than on MPD-I nanofiber. The observation that smaller diameter PCA fibers grew on MPD-I nanofiber suggests that enhanced evaporation rate of water at highly curved surfaces [9,10] (Kelvin effect) led to smaller areas of water on the

nanofiber surface than on the microfiber surface. Both fibers and spheres were observed on the flat glass substrate in other areas not shown in Fig. 7.

A filter of conventional structure can be made more efficient for the collection of small particles and droplets by growing nanofibers of PCA onto the surfaces of the larger fiber by the methods described in this paper. Growth of nanofibers onto very large polypropylene fibers (450 μm) provides an example. There is about a two or threefold increase in surface area for 0.3% increase in volume (Fig. 8). This estimate was based on the observation that PCA fibers formed on only half of the surface area of the polypropylene. The increase in surface area and increase in volume were estimated by counting the number of PCA fibers per unit area, the fraction of polypropylene fiber covered and the average length and diameter of a typical PCA fiber.

Various structures, including fibers, spheres, and branched fibers, were formed on a substrate as the local concentration of the cyanoacrylate vapor near the substrate was changed by heating the monomer at different temperatures. Heating at higher temperature resulted in an increased local concentration of the monomer, which resulted in large monomer droplets. At lower temperatures monomer concentration in the vapor was lower and small droplets were formed in the vapor [11]. PCA spheres were formed at high temperatures ($\geq 180^\circ\text{C}$) from larger monomer vapor droplets while smaller monomer

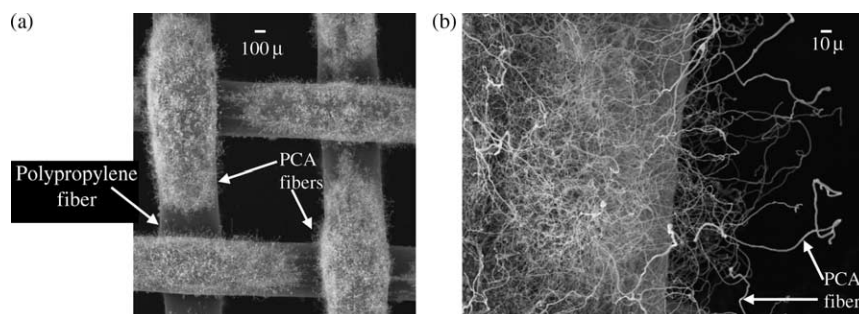


Fig. 8. (a) Scanning electron micrographs of patches of PCA nanofibers obtained after exposing a woven mesh of thick polypropylene fibers to water vapor and then to cyanoacrylate vapor. (b) Closer view of the PCA fibers formed. The temperature of monomer vaporization was 160°C and the exposure time was 1 h.

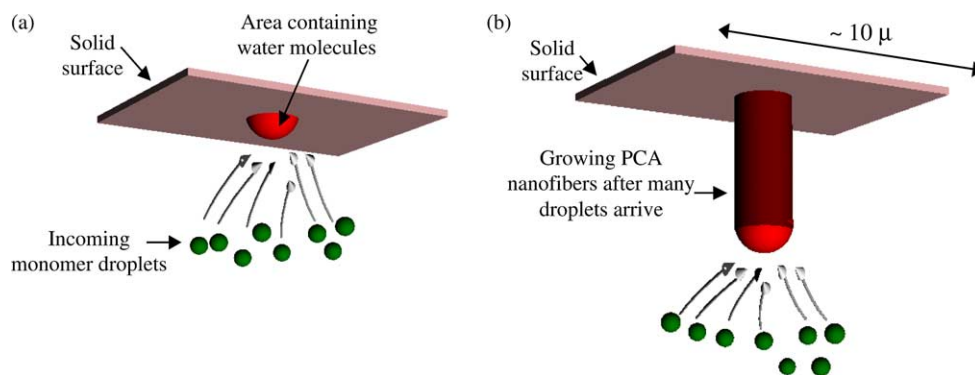


Fig. 9. Proposed model for fiber growth. (a) Fiber growth begins with an area, covered with water molecules, on a solid surface. The monomer droplets, add to these water molecules, are initiated and polymerized. (b) The water molecules on the growing tip of the fiber are then available to initiate the polymerization of the next droplet that arrives at the tip.

vapor droplets resulted in PCA fibers at lower temperatures (≥ 100 °C).

Fibers or whiskers are often grown by a process that involves a drop of catalyst fluid carried on the growing tip. The process is called a catalyst assisted, vapor-liquid-solid growth process (VLS) [12–14] and often used to produce crystalline fibers. In the VLS process, the diameter of the fiber is limited by the diameter of the liquid catalyst drop. The observations described in Fig. 5 led to the hypothesis that PCA fibers grow from tiny spots on the substrate where water molecules are present (Fig. 9(a)). Fig. 4 shows that the fibers grew longer, but not wider, with continued exposure to the monomer vapor. This observation suggests that the water molecules are carried at the tip, either as a patch of water molecules about one layer thick or as a small droplet with a shape controlled by surface tension. Monomer arriving at the tip was polymerized rapidly in the presence of water molecules. Monomer arriving at the sides of the fibers polymerized much more slowly, or disappeared by evaporation. PCA fibers described in this paper are not crystalline but the surface tension and volume of the water drop controls the diameter of the fiber as for crystals. Other related fiber growth processes include chemical vapor deposition [15–17] and reaction induced crystallization [18].

4. Conclusion

A technique for producing useful structures of polycyanoacrylate on various substrates was demonstrated. Tiny water covered areas provide a way to initiate the growth of polymer structures engineered on nanometer scales. The morphology and size of the structures can be controlled. These small structures with large surface area per unit mass promise to be useful in applications that depend on surface area. The results suggest that other polymerization systems controlled by

strategic placement of tiny quantities of initiator may also lead to interesting structures.

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