Facile catalytic growth of cyanoacrylate nanofibers

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High aspect ratio (>500), neat poly(ethyl 2-cyanoacrylate) nanofibers were synthesized catalytically by vapour phase polymerization under high relative humidity and ambient conditions.

Polymer nanofibers have been a subject of great interest due to their enormous potential application in a variety of fields that include nanofiber reinforced composites, filtration, tissue templating, wound dressing, cosmetics, protective clothing, electrical and optical applications.[1] The most promising techniques currently used to fabricate polymer nanofibers are (a) template-based synthesis[2] and (b) electrospinning.[1,3] The former method involves synthesizing the polymer chemically or electrochemically inside the pores of a template (*e.g.* anodized alumina membrane), or drawing a polymer melt into the pores by capillary action. The template then is sacrificed by dissolution to release the nanorods, nanowires or nanofibers. Furthermore the length of the nanostructures is limited by the template thickness. On the other hand electrospinning requires the polymer to be soluble in a suitable solvent or melt processible and also lacks control over the placement of the nanostructures. In this communication, we report novel catalytic growth of long nanofibers (>100 μm) of poly(ethyl 2-cyanoacrylate) without a template *via* vapour phase polymerization. Our results show that this method is versatile enough to promote in-place growth of nanofibers with relative ease and excellent reproducibility.

In this study we were interested in answering the question whether it was possible to cause spontaneous, self-sufficient, catalytic growth of polymer nanofibers during polymerization. To address this question we proposed an analogy between the growth mechanisms during two phase transition processes: crystallization from a melt and heterogeneous polymerization. The modified Avrami equation has been successfully applied to explain different morphologies such as rods (1-D), discs (2-D) and spheres (3-D) observed during polymer melt crystallization.[4,5] The equation defines the relationship between the growth of a polymer to a kinetic parameter such as time for each dimensional modality. During crystallization, nucleation and the growth rate of the crystals control the morphology of the polymer. This same analysis can be applied to heterogeneous polymerization wherein concentration of initiator and rate of initiation are the relevant processes that control the morphology of the polymer. This hypothesis is also evident in Iguchi and Murase's study.[6] They had observed variation in morphologies (plates and rods) of poly(oxymethylene) during its liquid-phase polymerization using different ratios of catalyst to co-catalyst concentrations. These variations were attributed to the differences in the rate and sites of nucleation for the different polymerization conditions. To investigate this hypothesis further, we chose to study the vapour phase polymerization of ethyl 2-cyanoacrylate (ECA), as the rate of this polymerization can be controlled effectively.

ECA, commonly known as Super Glue®, undergoes anionic polymerization by nucleophilic attack to form a mechanically strong polymer with excellent adhesive properties.[7] The single component adhesive is unique as it bonds to a variety of surfaces instantly under ambient conditions. This is attributed to the fact that ECA is polymerized readily by traces of water that are absorbed on virtually all types of surfaces. This rapid polymerization has also been used as an effective method for developing latent fingerprints by forensic scientists *via* a process known as cyanoacrylate fuming, wherein fingerprints left on a surface are subjected to fumes of ECA.[8,9] Polymerization of the cyanoacrylate by initiators in the fingerprint results in the formation of a white polymer residue that makes the ridges of the fingerprint visible. There are numerous techniques to enhance the development of the fingerprints for better identification.[10] Fuming in the presence of a relative humidity (RH) of 50–80% is known to accelerate the polymerization process. For the purpose of studying this rapid polymerization we utilized a simple fuming chamber† that allows for the catalytic growth of poly(ethyl 2-cyanoacrylate) on silicon substrates under different relative humidities. Our study showed that at very high RH, we not only have rapid polymerization of ECA, but also we form high aspect ratio nanofibers in large quantities and only on the crests of the fingerprint.

Fig. 1 shows a typical scanning electron micrograph of PECA grown on the ridges of the fingerprint on a silicon substrate in the fuming chamber at a RH greater than 95%. As seen in Fig. 1(a) and 1(b) the fibers do not grow between the ridges of the fingerprint, illustrating the in-place deposition of fibers only on areas where initiator was present. Fig. 1 (c) depicts an average area of fiber growth showing fibers that have diameters ranging from 100 nm up to 400 nm. However, interestingly, a majority of the fibers have their diameters in the 200–250 nm range. A magnified view of such a typical fiber is shown in Fig. 1(d). The length of the fibers was of the order of hundreds of microns implying aspect ratios in excess of 500. When this same experiment was repeated under low humidity (RH $< 30\%$) with other conditions the same, only film-like polymer or no polymer at all, was generated. This is in accordance with previous studies of this polymer growth on fingerprints that had low moisture content.[9] This same study observed 'noodle-like' structures on prints that had higher

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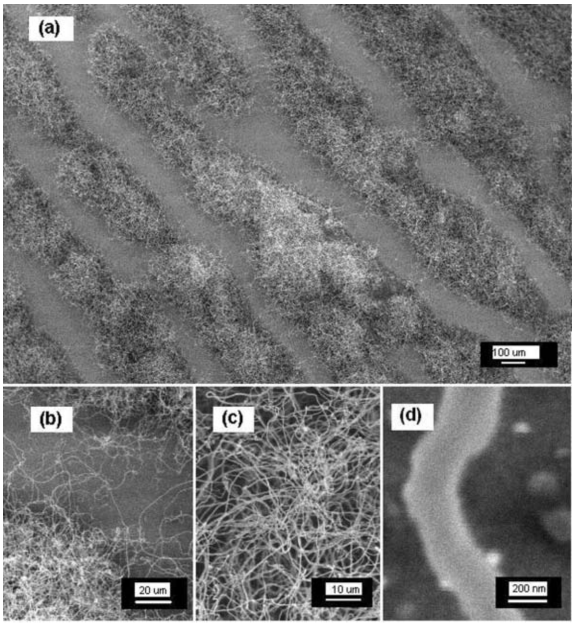

Fig. 1 SEM pictures of nanofibers of PECA grown on fingerprint ridges at 30 °C and relative humidity >95% over a period of 16 h. (a) Low magnification view. (b) Close-up view of the ridge pattern. (c) Close-up view of the nanofibers. (d) Magnified view of a single fiber.

moisture content. However, there was no control of humidity during their fuming process, thus it is highly imperative to maintain high humidity to obtain the nanofibers that we have observed. This agrees well with our hypothesis that by varying relative humidity we effectively varied the rate of polymerization thereby resulting in variation in the morphology of the polymer obtained.

This surprising result made us curious to investigate further the onset of the growth of these nanofibers. In Fig. 2 we show an SEM picture taken of the substrate surface at the very early stages of the reaction (<15 min of exposure to ECA–H_2O (v)). This set of micrographs clearly shows the development of the nanofibers, indicating that the catalytic growth of the polymer nanofibers has its genesis directly in the deposit of the fingerprint. Although, the fibers appear to be hollow they do have an inner core filling as seen in the top view of a single fiber stub (Fig. 2(b) inset). The deposit in the fingerprint has a complex composition of amino acids, urea, lactic acids, fatty acids and glycerides mixed together with inorganic constituents like chlorides, ammonia, sulfates and phosphates.[11] The polymerization of cyanoacrylate proceeds anionically, so several constituents in the fingerprints such as chlorides, moisture, carboxylic acid ions and amines can act as nucleophilic initiators to trigger polymerization.[12] To elucidate the exact initiator in the fingerprints that forms these nanofibers, we subjected a single initiator at a time to similar reaction conditions.† Sodium chloride, stearic acid, palmitic acid and amino acids spin coated from solution on the substrate surface resulted in the growth of short nanofibers but they sparsely populated the surface and did not resemble the neat nanofibers we observed on the fingerprint. These results indicated that the growth of high aspect ratio, densely populated nanofibers arises from the complex composition of fingerprint interacting with the monomer vapour at high humidity. The non-initiating components of the fingerprint at high humidity play a major role in dispersing the initiators to favor the formation of the nanofibers. To synthetically mimic the deposit of the fingerprint we then prepared a mixture of a non-initiating component, linoleic acid, and a known initiator, aqueous sodium chloride. On subjecting this synthetic mixture to the fuming conditions, we were able to successfully fabricate the long, high aspect ratio (>500), nanofibers that we had previously observed (see Fig. 3). The role played by the presence of the non-initiating components in the mixture is not completely understood and more experiments are underway to elucidate the mechanism. Our investigation, however, thus far implies that we can controllably create a network of polymer nanofibers where we want them—for example by stamping an "ink" of the synthetic mixture at specific positions and in specific patterns on a surface, or by applying the initiator matrix to uneven surfaces by simple spraying—expanding the verstality of this technique.

The single initiator studies yielded another interesting observation with regard to the morphology of the polymer formed using different initiators under the same reaction conditions. Initiation by sodium hydroxide, potassium hydroxide and potassium acetate, resulted in a film with an interesting morphology; the film was involuted and seemingly bicontinuous with 'tortellini-like' features as seen in Fig. 4. By contrast, spheres of polymer were obtained when initiation was done with ammonium hydroxide. The formation of these different morphologies implies that the 1-D (fiber), 2-D (film) and 3-D (sphere) growth mechanisms during polymerization can occur with different initiators. Such behavior can again be explained by our hypothesis because by varying the

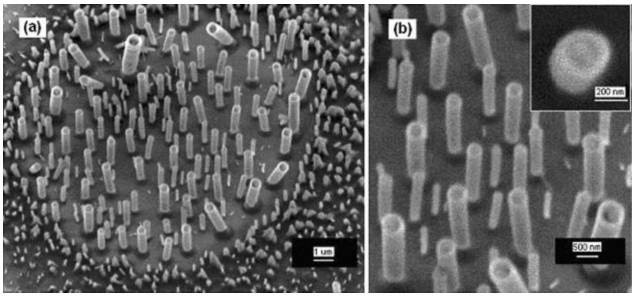

Fig. 2 Snapshot of initial polymer fiber (15 min exposure to monomer and high humidity) growth on a fingerprint at 30 °C and relative humidity >95%. (a) Low magnification view. (b) Close-up view of the same (inset showing the top view of fiber).

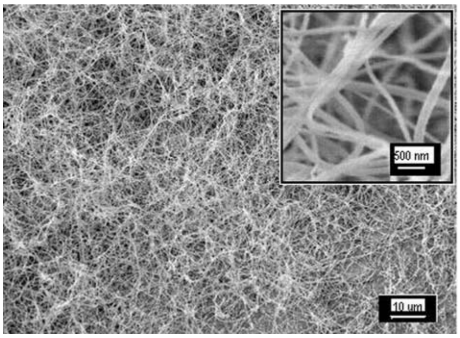

Fig. 3 PECA nanofibers obtained by initiation with the synthetic mixture of linoleic acid and aqueous sodium chloride (inset showing the same area at a higher magnification).

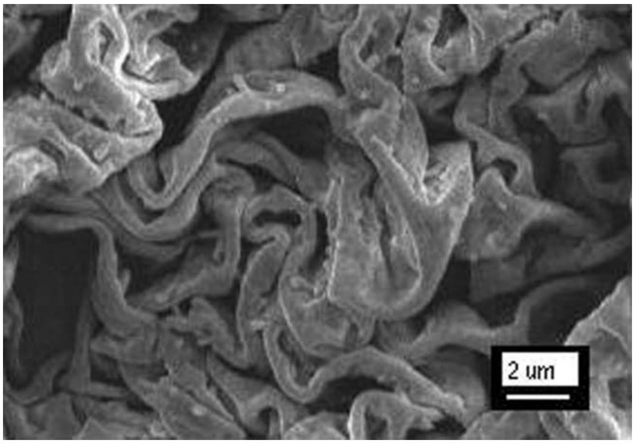

Fig. 4 Tortellini-like PECA film obtained by initiation with sodium hydroxide.

type of initiator we then altered the rate of initiation thereby resulting in the observation of the different morphologies. This implies that for the appropriate choice of reaction conditions and initiators we can controllably fabricate the required morphology of the polymer. Quartz crystal microbalance studies of the kinetics of polymerization of ECA using the different initiators and reaction conditions will be carried out to determine the rates required for the formation of the different morphologies.

In conclusion, we have demonstrated a facile, template-less, catalytic route to synthesizing PECA nanofibers. We were able to develop a synthetic mixture of the initiator to catalyze the formation of masses of nanofibers only on designated 'inked' areas. By varying the reaction conditions or initiator type we obtained different polymer morphologies suggesting that for appropriate initiation and reaction conditions this template-less technique for nanofiber formation can potentially be applied as a model for other polymer systems.

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Notes and references

† Cyanoacrylate fuming for fingerprints: a fuming chamber (oven) was maintained at 30 °C and humidified to a RH > 95% by placing an appropriate amount of water in a beaker in the chamber. A silicon substrate was cleaned using a piranha etch (3 parts sulfuric acid to 1 part hydrogen peroxide), dried and then imprinted with a fingerprint. The substrate was then placed in the chamber along with a dish containing approximately 1.5 g of liquid ECA (CVS Pharmacy). Two fans inside the oven provided sufficient circulation in the gas phase. Reaction was allowed to proceed for 16 h at 30 °C. For low humidity (RH < 30%) the experiment was carried out without the beaker of water in the chamber. Humidity was monitored by a hygrometer (Fisher Scientific). Single initiator studies were carried out in the same fuming chamber. Solutions of initiators were spun coated and dried on clean Si wafers before placing them in the chamber.

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