

Polymerization at the Gas/Solution Interface: Preparation of Polymer Microstructures with Gas Bubbles as Templates

Maciej Mazur, Anna Frydrychewicz

Department of Chemistry, Laboratory of Electrochemistry, University of Warsaw, 02-093 Warsaw, Pasteura 1, Poland

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ABSTRACT: We report on the chemical polymerization of 2-methoxyaniline at the interface between an aqueous solution and air. The polymer is formed in the interfacial region, whereas the soluble trimer is yielded in the bulk of the polymerization solution. The preferential polymerization of 2-methoxyaniline is discussed in terms of monomer and oligomer accumulation at the interface, which influences the reactivity of these species and allows further polymerization. The phenomenon of polymer growth is employed to selectively deposit polymeric material onto glass slides decorated with gas microbubbles. Because of preferential polymerization at the bubble/solution interface, hemispherical features are produced on the surface of

glass. When some polymeric material is mechanically removed, microrings or microholes are obtained. The anomalous polymerization of 2-methoxyaniline is compared to that of 2-methylaniline. This monomer polymerizes uniformly within the entire volume of the reaction mixture; thus, no preferential polymer formation at the gas/solution interface is observed. As a result, deposition on microbubble-decorated glass slides produces polymeric films containing a number of microholes. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 2169–2176, 2007

Key words: conducting polymers; microstructure; templates

INTRODUCTION

The development of microstructured and nanostructured materials has drawn increasing attention in recent years because of their potential applications in catalysis, nanoelectronics, drug delivery, and chemical analysis. Among other reasons, microstructures and nanostructures prepared from conducting polymers are of special interest because they reveal remarkable optical, mechanical, and electrical properties.¹

Polymeric microstructures can be prepared by a variety of methods, template synthesis being one of the most successful.^{2–9} The synthesis involves the use of natural or fabricated templates that direct the deposition of the desired material into structures determined by their shape and geometry. Examples of templates used in the synthesis of nanostructured and microstructured polymers include ion-track-

etched polycarbonate membranes and porous materials (e.g., aluminum oxide membranes). They allow the preparation of tube or fiber structures with a well-defined geometry and morphology.¹⁰ Recently, Shi's group and others^{11–18} have reported on the use of gaseous microbubbles in the synthesis of a variety of structures of unusual morphologies, including microcontainers, microwhiskers, and microbottles.

In this article, we demonstrate for the first time the deposition of poly(2-methoxyaniline) onto microbubble-decorated glass with electroless polymerization.^{19–26} Because of preferential deposition at the gas/solution interface, hemispherical structures are obtained. These structures can be easily transformed into microrings or microholes by the mechanical removal of some loosely bound polymeric material. We discuss the details of 2-methoxyaniline polymerization in the interfacial region and propose a mechanism for microstructure formation at the glass substrate. These results are compared with the polymerization behavior of 2-methylaniline, which is not preferentially formed at the gas/solution interface.

EXPERIMENTAL

Chemicals

All chemicals were of the highest quality commercially available: 2-methoxyaniline (Aldrich, St. Louis,

Correspondence to: M. Mazur (mmazur@chem.uw.edu.pl).

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MO; >99%), 2-methylaniline (POCh, Gliwice, Poland; reagent-grade), ammonium peroxodisulfate [(NH₄)₂S₂O₈; Fluka, St. Louis, MO; >98%], hydrogen peroxide (Chempur, Piekary Slaskie, Poland; 30%), hydrochloric acid (POCh; 36%), perchloric acid (POCh; 70%), and chloroform (POCh, Gliwice, Poland; reagent-grade). Aqueous solutions were prepared from water of high purity (Milli-Q, Billerica, MA).

Instrumentation

Optical spectra were recorded with an ultraviolet-visible (UV-vis) spectrophotometer (UVMini-1240, Shimadzu, Kyoto, Japan). IR spectra of polymers and oligomers in KBr pellets were measured with a Shimadzu 8400 Fourier transform infrared (FTIR) spectrometer (Kyoto, Japan).

An electrospray ionization mass spectrometer (LCT Micromass, Milford, MA) was used to record the mass spectra of the oligomeric species.

Gel permeation chromatography was performed with a LabAlliance chromatograph (State College, PA) calibrated with polystyrene standards.

Scanning electron microscopy (SEM) images were taken with a Leo 435 VP microscope (Oberkochen, Germany) on samples sputter-coated with palladium/gold. Optical images were recorded with a USB IntelPlay optical microscope (Santa Clara, CA).

The surface tension of aqueous solutions of 2-methoxyaniline was measured with a Nima ST 9000 tensiometer (Coventry, England).

Polymer synthesis

For polymer synthesis, 2 cm³ of an aqueous 0.36M monomer (2-methoxyaniline or 2-methylaniline) solution in 1M HCl or HClO₄ was added to 2 cm³ of 0.4M (NH₄)₂S₂O₈ in 1M HCl (or HClO₄) and stirred for a couple of seconds. Then, the solution was left for a specified time to allow polymer formation. The polymerization was carried out at room temperature.

Preparation of oxygen microbubbles on glass slides

Planar glass slides were placed on a round clock glass. Then, a solution prepared by the mixing of 1 cm³ of 0.1M H₂O₂ with 1 cm³ of 0.1M (NH₄)₂S₂O₈ in 1M HCl (or HClO₄) was poured onto the round clock glass and left for 10 min. The oxygen microbubbles were formed at the bottom side of the glass slide.

Deposition of polymers onto a bubble-decorated surface

A freshly mixed solution containing a monomer [1 cm³ of 0.72M monomer with 1 cm³ of 0.8M (NH₄)₂S₂O₈ in 1M HCl or HClO₄] was added to the round clock glass (on which a bubble-decorated glass slide was placed) and gently mixed with a micro-

pipette. The solution was left for about 10 or 15 min to allow polymerization. Then, the glass slide was removed from the solution, rinsed with water, and dried.

RESULTS AND DISCUSSION

Preparation of a polymeric layer at a solution/gas interface

For the majority of the monomers reported in the literature, a chemically produced conducting polymer is obtained in the form of a suspension dispersed in a solution.²⁷⁻²⁹ A typical example of such behavior is shown by 2-methylaniline, which is uniformly polymerized in the entire volume of the solution. This can be confirmed by the registration of the UV-vis absorption spectra of the suspension. In Figure 1(a), spectra recorded 1, 10, 20, and 30 min after the mixing of the solutions of the monomer and oxidant are shown. The formation of the polymer starts after about 20 min and is followed by rapid precipitation in the solution. This is indicated by the appearance and fast increase of absorption bands at about 700 and 900 nm. These bands are attributable to polarons and bipolarons that form in the polymeric backbone.³⁰

This typical behavior is not observed for 2-methoxyaniline. The polymer is formed preferentially at the liquid/air interface, whereas a soluble brownish-red product is produced in the solution. We have studied the formation of both soluble and polymeric products with UV-vis spectroscopy. The experiments have been performed for two cases: (1) the light beam passes through the aqueous phase containing the soluble product and (2) the light goes through the polymeric layer (Scheme 1). In Figure 1(b), the successive spectra of the soluble product are presented. A growing absorption band with a maximum at about 420 nm is visible. Such a band is characteristic of short oligomeric species produced in a solution.^{31,32}

When the light beam in the UV-vis experiment passes through both the polymeric layer and bulk solution [Scheme 1(b)], the spectra reveal two broad absorption bands at about 450 and 850 nm that increase with the reaction time [Fig. 1(c)]. The band at 850 nm [similar to the bands at 700 and 900 nm for poly(2-methylaniline)] can be assigned to polarons/bipolarons that form in the polymeric backbone.³³⁻³⁸ Thus, its presence in the spectrum confirms the formation of the polymer at the liquid/air interface. The band at 450 nm must derive from the overlap of the 420-nm band of oligomers present in the solution and the (second) band of the polymer at a slightly higher wavelength.

To gain a deeper understanding of the chemical nature of the soluble products of 2-methoxyaniline oxidation, we extracted these species with chloroform and studied them with electrospray ionization mass

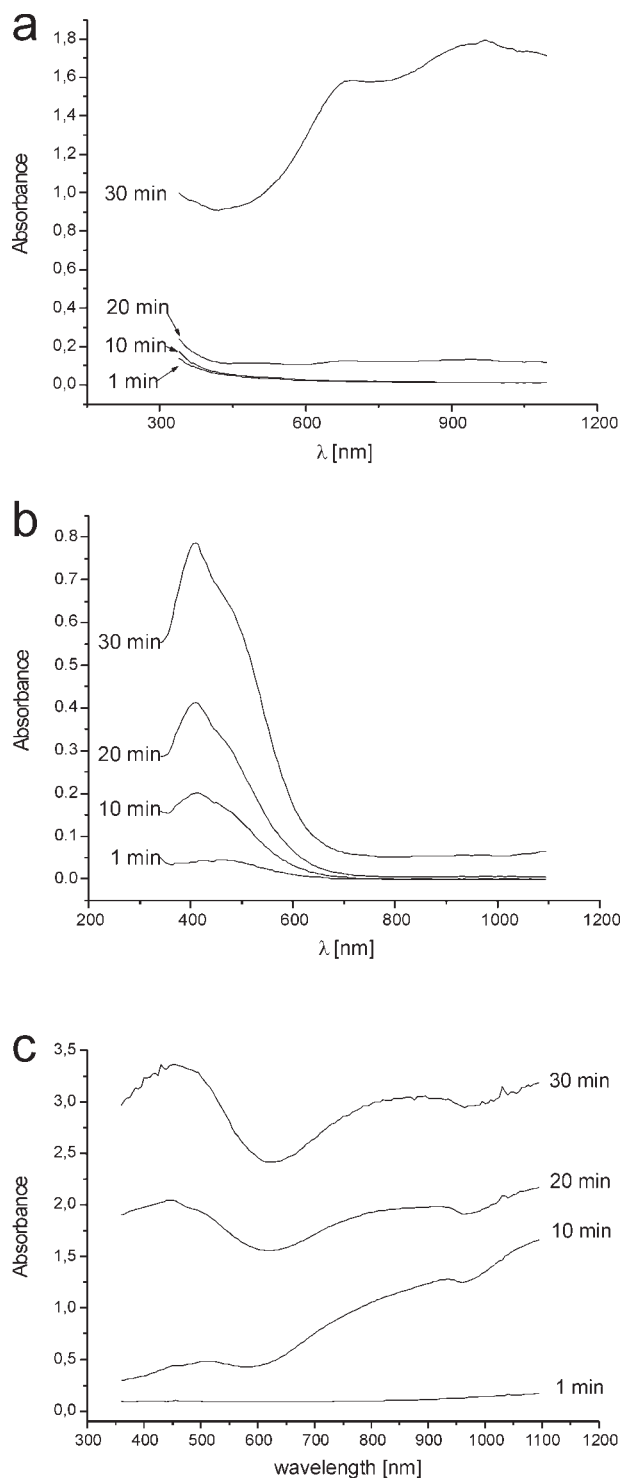
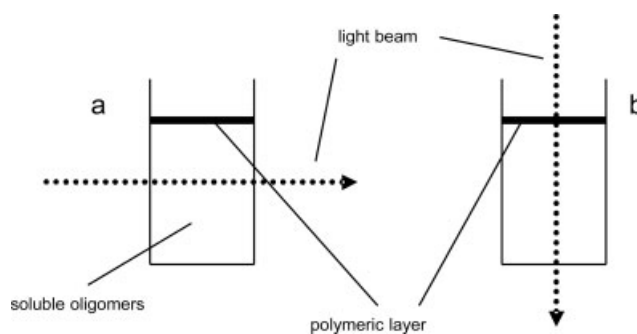


Figure 1 (a) Dependence of UV-vis spectra of poly(2-methylaniline) precipitated from a solution containing the monomer and the oxidant on the polymerization time (1M HClO₄ solution), (b) dependence of UV-vis spectra of 2-methoxyaniline oligomers formed in the bulk of a solution on the reaction time (1M HClO₄ solution), and (c) dependence of UV-vis spectra of poly(2-methoxyaniline) forming at the solution/air interface on the polymerization time (1M HClO₄ solution).

spectrometry. The mass spectrum obtained is presented in Figure 2(a). The most prominent peak in the spectrum occurs at 364 m/z and ideally corresponds to a protonated oxidized form of the 2-methoxyaniline linear trimer $[(M_3 + H)^+]$. This peak might also be attributed to some higher oligomers, such as hexamers $[(M_6 + 2H)^{2+}]$ and nonamers $[(M_9 + 3H)^{3+}]$. However, this scenario is rather unlikely because these molecules seem to be insoluble in an aqueous solution. Therefore, we assume that the 364 peak is attributable to a linear trimer of 2-methoxyaniline. In the spectrum, a significant number of $(M + H)^+$ ions at 124 m/z are also detected that correspond to monomeric 2-methoxyaniline.

The presence of trimers in the reaction mixture suggests that they are the most stable species produced in the solution. The odd number of mers in the oligomeric chain may derive from a specific mechanism of monomer recombination different from that of aniline and some other aniline derivatives (e.g., 2-methylaniline). It is well established that aniline is oxidized to radical cations, which undergo recombination to dimers. These dimers are further oxidized and recombine to tetramers and so on.^{39,40} The odd-number oligomers are also produced but at significantly lower rates than those with an even number of mers in the chain.⁴¹ The presence of trimers as the main products of 2-methoxyaniline oxidation may reflect the fact that after the formation of dimers, they react with the monomers. The reason for such a mechanism could be the presence of an electron-donating methoxy group in the benzene ring. This substituent reveals an activating influence on the reactivity of the monomer, so the reaction of a dimer with the monomer is more likely than the recombination of two dimers.

The question now arises of what the reason is for the increased stability of 2-methoxyaniline trimers. The oxidized form of a trimer should contain one quinoid unit located in the middle of the chain and two benzenoid units at the two ends of the oligomer. For a dimer or higher even-number oligomers, a quinoid



Scheme 1 Scheme of the UV-vis experiment: (a) the optical beam from the spectrometer passes through the solution of 2-methoxyaniline oligomers and (b) the optical beam passes through the polymeric film and the solution.

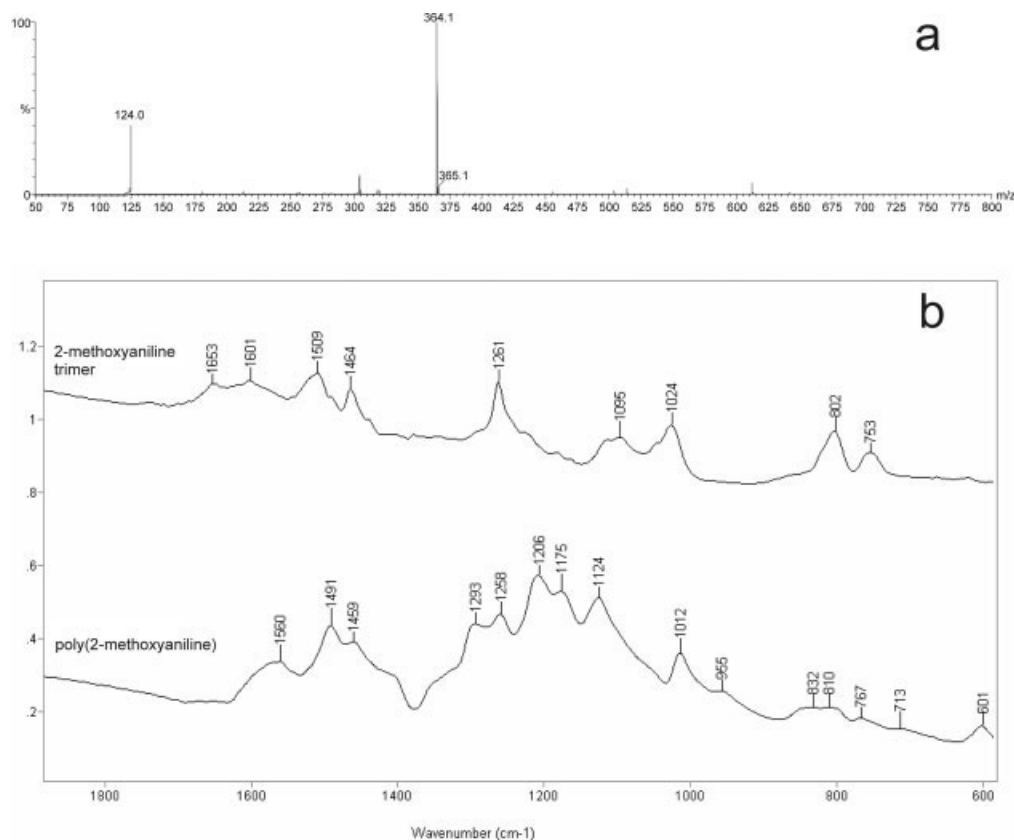


Figure 2 (a) Time-of-flight electrospray ionization positive mass spectrum of 2-methoxyaniline oligomers (prepared in a 1M HCl solution) and (b) FTIR spectra of 2-methoxyaniline oligomers and poly(2-methoxyaniline) (prepared in a 1M HCl solution).

unit is always located at one end of the chain with reactive imine functionality. Thus, the even-number oligomers are reactive and follow further oligomerization, whereas the odd-number oligomers (trimers) are stable as they contain much less reactive benzenoid units at two ends of the chain.

The formation of quinoid structures in 2-methoxyaniline trimers (extracted with chloroform) has been confirmed by IR spectroscopy [Fig. 2(b)]. The bands at 1653 and 1464 cm^{-1} can be attributed to a C=N stretching vibration in the quinoid unit⁴² and a C=C stretching vibration of the quinoid ring,⁴³ respectively. The presence of benzenoid-type rings is confirmed by a C=C vibration at 1509 cm^{-1} .⁴⁴ A signal at 1601 cm^{-1} is attributable to N—H deformation in the —NH₂ group^{42,45} of the trimer (or the monomer, which is also present in the reaction mixture).

The IR spectrum of the polymer (formed at the air/solution interface) shown in Figure 2(b) reveals typical signals reported previously for electrochemically generated poly(2-methoxyaniline).⁴⁶ In comparison with the IR spectrum of oligomeric species, the C=N stretching vibration signal for the polymer occurs at 1560 cm^{-1} , and this reflects the fact that semiquinoid (not fully oxidized) units are present in the polymer backbone.⁴⁴ Also, the signal attributable to the N—H

deformation vibration at 1601 cm^{-1} is absent in the spectrum, and this suggests a lack of a large number of free —NH₂ groups.

We further aimed to determine the chain length of the polymeric product with gel permeation chromatography. The material was collected and deprotonated in an NH₃ solution and then was dried and dissolved in tetrahydrofuran (THF). Because the product was only partially soluble in THF, we were able to study only the low-molecular-weight fraction of the product. The gel chromatogram [Fig. 3(a)] indicates that the mass of the macromolecules is in the range of about 600–10,000 g/mol (number-average molecular weight = 2640 g/mol), which corresponds to about 5–80 mers in the chain. Therefore, the length of the chains is relatively short, but from our point of view, the important information is that it is considerably longer than that of the water-soluble product (trimer).

These results allow us to draw some general conclusions related to the chemical oxidation of 2-methoxyaniline and the polymerization process. It appears that 2-methoxyaniline monomers are oxidized into radical cations, which recombine, forming unstable reactive dimers. These dimers react preferentially with monomers to produce stable trimers in the bulk of the solution. However, simultaneously, a

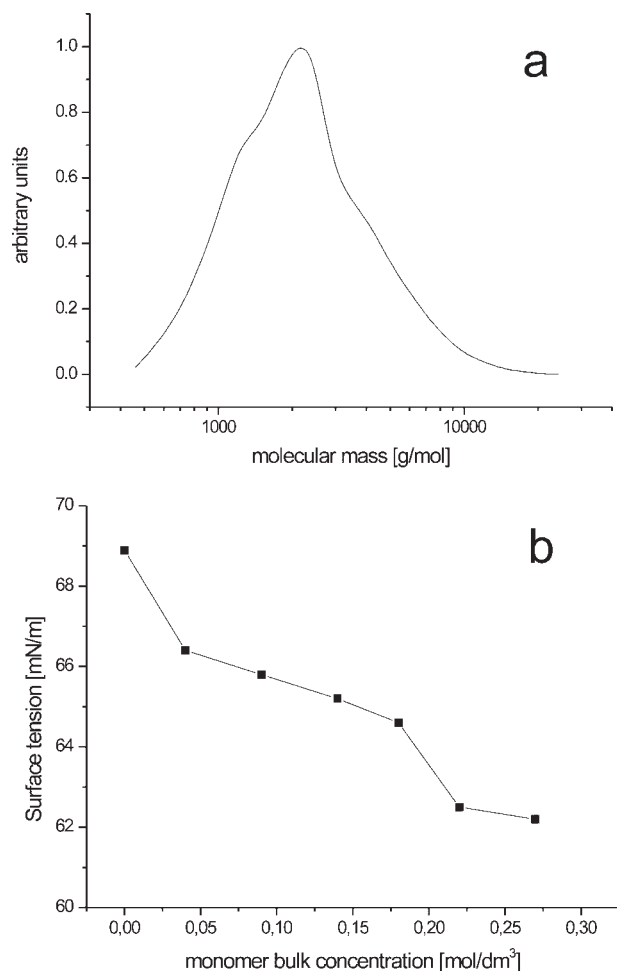


Figure 3 (a) Gel permeation chromatogram of poly(2-methoxyaniline) prepared in an HCl solution and (b) surface tension versus the molar concentration of 2-methoxyaniline in an aqueous 1M HCl solution.

polymeric film is produced at the air/solution boundary. The reason for the formation of the polymeric material needs to be clarified. The fact that the polymer is created at the air/solution boundary suggests that trimers and monomers may accumulate in the interfacial region and as a result of an increased local concentration follow the polymerization reaction. To verify whether 2-methoxyaniline is accumulated at the air/solution boundary, we have determined the surface tension of the solution as a function of the monomer bulk concentration (Fig. 3). On the basis of the Gibbs isotherm,⁴⁷ we can estimate the surface excess of 2-methoxyaniline to be about 1.7×10^{-10} mol/cm² (for a bulk concentration of 0.18 mol/dm³). This value suggests that a significant accumulation of monomers occurs at the solution/air interface, and this may be responsible for the preferential formation of the polymer (in our previous article,⁴⁸ we report that an increased local concentration of the monomers in the bulk of the solution results in the formation of polymeric particles⁴⁸). In fact, in the reaction mixture,

not only monomers but also trimers are likely accumulated at the interface as they should be less soluble in an aqueous solution than the monomers. At this stage, we can only hypothesize that an accumulation of trimers may change their geometry and thus reactivity. As a result, these species are much more reactive in the interfacial region than in the bulk of the solution and easily follow further polymerization.

Deposition of polymers onto a bubble-decorated surface

With an understanding of the methoxyaniline polymerization mechanism, we are ready to study the selective deposition of polymers onto surfaces decorated with gas microbubbles.

We produced oxygen bubbles on glass slides, using an aqueous acidic solution containing oxygen peroxide and ammonium persulfate. Because of the higher normal potential of the persulfate/sulfate redox pair, oxygen peroxide was oxidized into gaseous oxygen:

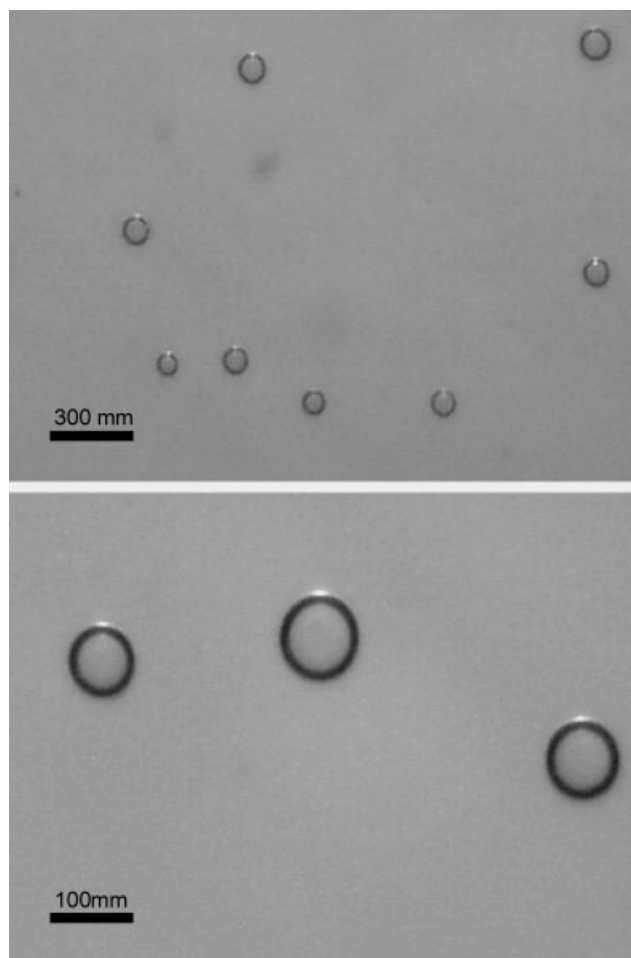
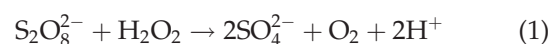


Figure 4 Optical micrographs of microbubbles deposited onto a glass substrate (prepared in a 1M HCl solution).

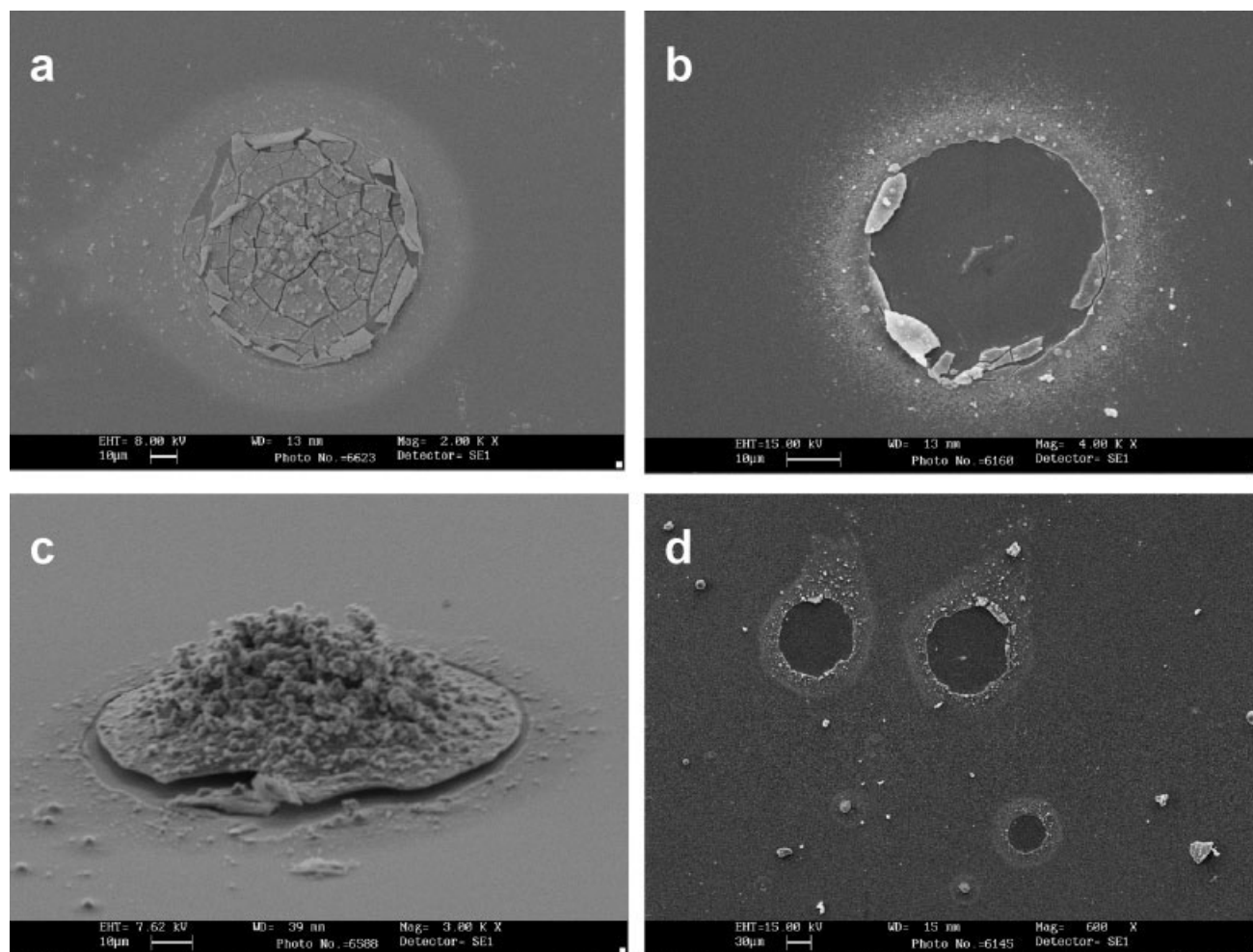


Figure 5 SEM images of poly(2-methoxyaniline) microstructures deposited onto glass (prepared in a 1M HCl solution): (a) a collapsed hemisphere (deposition time = 10 min; scale bar = 10 μm), (b) a microring (loosely bound material was removed; deposition time = 10 min; scale bar = 10 μm), (c) a saucerlike structure (deposition time = 15 min; scale bar = 10 μm), and (d) microholes in the polymeric layer (loosely bound material was removed; deposition time = 10 min; scale bar = 30 μm).

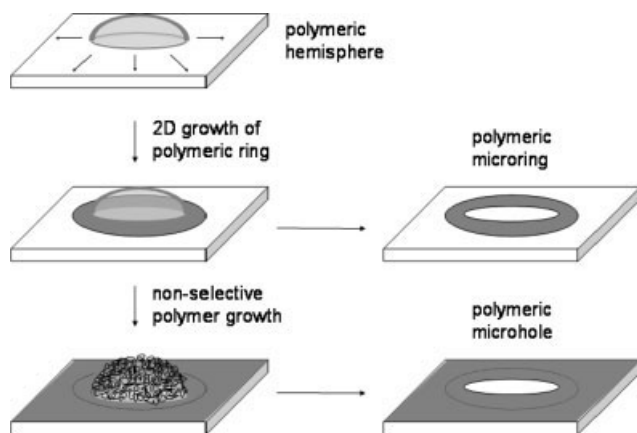
In the procedure that we used, two solutions containing persulfate and peroxide were mixed and immediately poured into a vessel in which a glass slide had been placed. The reaction was allowed to proceed for 10 min, and the microbubbles accumulated under the glass slide. In Figure 4, we show optical microscopy images of oxygen bubbles formed under the glass slide immersed in the persulfate/peroxide solution. The typical size of the bubbles was about 80 μm , and their surface concentration was about 2×10^3 bubbles/ cm^2 .

We further deposited poly(2-methoxyaniline) through the addition of a solution containing 2-methoxyaniline and the oxidant (ammonium persulfate). After a specified time (10 or 15 min), the glass substrate was removed from the reaction mixture, gently rinsed with distilled water, and dried. The polymer deposits were then studied with SEM.

In Figure 5(a), we present the SEM image of a polymeric microstructure obtained through the deposition of poly(2-methoxyaniline) onto an oxygen bubble

(polymerization time = 10 min). One can see a round structure with a diameter of about 140 μm . The outer part of the structure forms a thin ring that adheres well to the surface of the glass. The inner part consists of cracked fragments of the polymeric film. It seems that a continuous polymer layer at the bubble/solution interface is produced during the deposition, but after drying, it collapses and cracks into pieces. These polymeric fragments can be removed from the surface by extensive rinsing with water. When the unbound material is detached, a polymeric ring is left on the surface, as shown in Figure 5(b).

With an increase in the reaction time, the polymer starts to deposit nonselectively both at the bubble sites and on bare glass. In Figure 5(c), we show a polymeric saucerlike feature produced after 15 min of deposition. It appears that the microstructure is formed by the growth of an amorphous, globular material on a polymeric layer at the bubble/solution interface (hemisphere). The polymer is also deposited in the form of a thin film on bare glass. As a result,



Scheme 2 Possible mechanism of poly(2-methoxyaniline) microstructure formation.

when the loosely bound saucerlike structure is removed by extensive rinsing of the sample with water, a polymeric layer containing holes is obtained, as shown in Figure 5(d).

These microscopy observations suggest the following scenario for bubble-assisted polymer growth (Scheme 2). The polymer is initiated at the bubble/solution interface, forming a hemisphere. Then, two-dimensional radial growth occurs, resulting in the formation of a ring surrounding the hemisphere. When the reaction time is increased, the polymer starts to grow nonselectively on the whole substrate, both on the hemispheres (in the form of a globular, amorphous polymer) and on bare glass (in the form of a thin film). The polymeric material that forms at the bubble/solution interface, when dried, is mechanically unstable and cracks into loosely bound pieces. These pieces can be easily removed by the substrate being splashed with water. As a result, microring or microhole structures are obtained, depending on the polymerization time.

The formation of poly(2-methoxyaniline) microrings is possible for two reasons: the polymer is preferentially produced at the gas/solution interface, and its growth is inhibited on bare glass (the inhibition of polymer growth on nonconducting substrates is discussed in ref. ³⁵). It is interesting at this point to examine the deposition of poly(2-methylaniline) on a microbubble-modified surface. 2-Methylaniline is polymerized within the entire volume of the reaction mixture; thus, we should not expect preferential deposition at the bubble/solution interface. However, it is likely that it will accumulate at the substrate surface (glass) similarly to polyaniline.⁴⁹ If this is the case, the polymer should deposit on bare glass with the exception of areas occupied by oxygen microbubbles. We deposited poly(2-methylaniline) onto a bubble-modified substrate and imaged the resulting structures with SEM (Fig. 6). A polymeric layer con-

taining a number of holes can be seen. The distribution and diameter of the holes correspond well to the amount and size of the oxygen microbubbles. It is obvious, therefore, that poly(2-methylaniline) produces a layer on the glass surface, but it is not deposited onto bubble sites, as they block the access of the polymer to the surface.

CONCLUSIONS

We have shown that poly(2-methoxyaniline) is polymerized preferentially at the interface between air and the solution containing the monomer and oxidant. This enhanced growth likely originates from the accumulation of the monomers and oligomers in the interfacial region, which alters their reactivity and as a result promotes polymerization. The unique polymerization behavior of 2-methoxyaniline allows the selective deposition of the polymer onto a gas-bubble-modified solid substrate. The resulting structures include microrings or microholes, depending on the

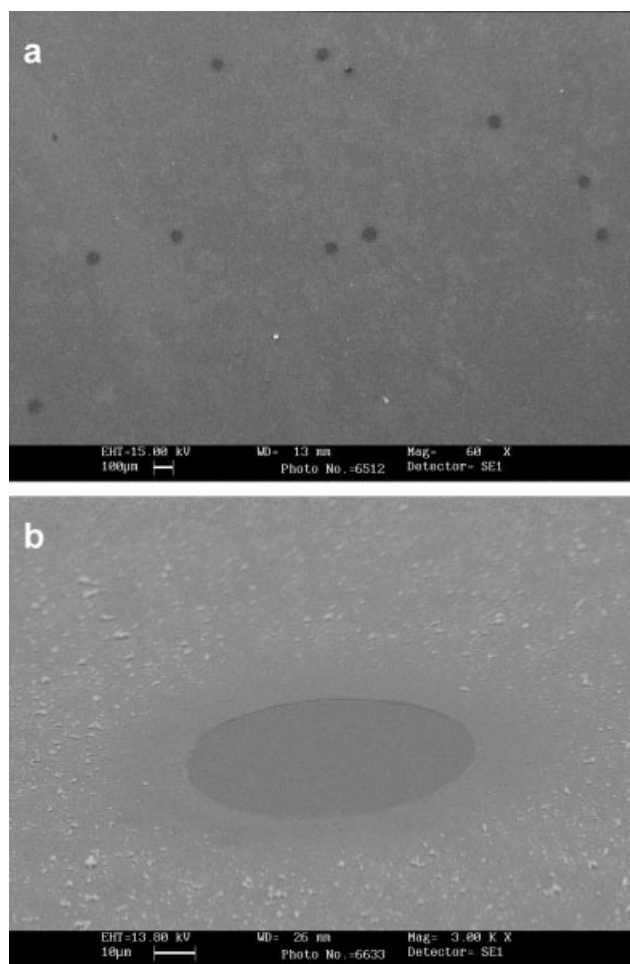


Figure 6 SEM images of poly(2-methylaniline) microholes prepared on glass (synthesized in a 1M HCl solution) with deposition times of (a) 10 (scale bar = 100 μm) and (b) 15 min (scale bar = 10 μm).

experimental conditions. The dimensions of the polymeric features perfectly match the diameters and distribution of the bubbles.

The use of gas bubbles appears to be a new promising template method in material synthesis. It is believed that it will find multiple applications in the preparation of patterned surfaces for a variety of purposes ranging from chemical analysis to biosensor devices and the construction of microelectronic elements. We are working now on further optimization of bubble-guided synthesis with the final goal of preparing structures with nanometer dimensions.

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