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Photoinitiated Interfacial Cationic Polymerization

Anders Hult,[†] Scott A. MacDonald, and C. Grant Willson*

IBM Research Laboratory, San Jose, California 95193. *Received December 10, 1984*

ABSTRACT: A new technique is reported for surface modification of polymers that is based upon photoinitiated cationic polymerization. The bulk, host sample is doped with a small amount of a cationic photoinitiator and exposed to radiation, thus creating a catalytic surface that, when exposed to an appropriate monomer, serves to initiate polymerization, thereby altering the surface properties of the bulk sample. The polymerization process is characterized by highly nonlinear growth kinetics. The effect of reaction variables on these kinetics has been explored and a molecular level model for the process is proposed.

In many applications of polymer materials, the chemical and physical properties of the surfaces are as important as the properties exhibited by the bulk material. This realization has stimulated several groups to develop methods for chemical modification of the surface of polymers.[1] The most common surface modification technique involves electron beam or γ irradiation of the sample followed by free radical initiated, graft polymerization.[2]

Surface modification via grafting reactions has been performed both in situ, by irradiation of the polymer surface in the presence of a reactive monomer, and by preirradiation followed by exposure to monomer in a subsequent step. The grafting reaction has, in turn, been carried out in two ways. Either the irradiated sample has been transferred in vacuo to a chamber in which the grafting reaction takes place[3] or it has been exposed to oxygen during or immediately after the irradiation. This latter process results in the formation of intermediate peroxides and hydroperoxides on the polymer surface which can be subsequently thermolyzed to form alkoxy radicals that function efficiently in the initiation of graft polymerization.[4]

Radiation-induced free radical graft polymerization has also been accomplished with UV light. Here, polymer samples were irradiated in a solution containing a vinyl monomer and a photosensitizer[5] or were irradiated after the surface of the sample was saturated with such a solution.[6] There are a few reports describing high-energy radiation-induced, ionic graft polymerization.[7,8] Evidence for an ionic mechanism is generally the successful grafting of a monomeric species, such as a vinyl ether, that is not prone to radical-initiated polymerization.

In the present work, we report a novel technique for surface modification of polymers that is neither grafting, in the usual sense, nor free radical in mechanism. We have studied a deposition technique that is based upon photoinitiated cationic polymerization. Here, the bulk sample is doped with a small amount of a soluble cationic photoinitiator. Exposure of the sample to UV light or high-energy radiation creates a strongly acidic surface due to radiolysis of the photoinitiator. After radiolysis, the sample is exposed to an appropriate monomer either in solution or in the gas phase. The photogenerated acid serves to initiate cationic polymerization of the monomer, thereby altering the surface properties of the bulk sample. An advantage of this technique is that the irradiated samples need not be handled in vacuo, UV exposures are routinely carried out in air and polymerization onto the surface from the gas phase has been successfully carried out hours after the exposure step.

The cationic photoinitiators that are most effective for this application are various onium salts. The existence of these onium salts has been known for nearly a century. The iodonium salts were first reported by Hartmann and Meyer in 1894[9] and the sulfonium salts first reported by von Halban in 1909.[10] Seventy years passed before the utility of these substances as cationic photoinitiators was realized. Now, a wide range of thermally stable photoinitiators based on diaryliodonium[11-13] and triarylsulfonium[14,15] salts of nonnucleophilic, complex metal halides have been prepared and tested. Irradiation of these compounds results in cleavage of a carbon-iodine[16] or carbon-sulfur[17] bond to generate a reactive radical cation. The radical cation abstracts hydrogen from its environment to ultimately form a stable, long-lived, strong Brønsted acid. The photogenerated acid can then be employed in the initiation of a variety of cationic polymerization processes. Although there are many monomer structures that undergo acid-catalyzed polymerization,[18] we have focused on simple vinyl ethers since these compounds are known to only undergo cationic or coordination polymerization and are inert to radical initiation.

The new surface modification technique is characterized by interesting and highly nonlinear polymer film growth kinetics. The film growth can be conveniently divided into three distinct phases. There is a short induction period, followed by rapid film growth, and finally a dramatic decrease or plateau in the polymerization rate. We have established a sensitive method for studying the kinetics of this process and have carried out experiments designed to provide insight into the factors that control the three stages of the reaction, i.e., the induction, the rapid growth region, and the plateau phenomenon.

Experimental Section

Materials. 2-Methoxypropene and *p*-methoxystyrene were purchased from Aldrich Chemical Co.; *p*-methoxystyrene was freed from inhibitor on a neutral aluminum oxide column before use, while 2-methoxypropene was used as received. Vinyl methyl ether, obtained from Matheson Inc., was also used as received. Poly(*p*-methoxystyrene) was prepared by free radical polymerization, purified by precipitation, and has $M_n = 68000$ and $M_w/M_n = 1.6$.

[†] Current address: Department of Polymer Technology, Royal Institute of Technology, Stockholm, Sweden S-10044.

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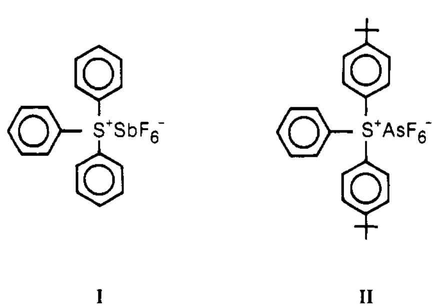

Figure 1. Onium salts I and II.

Polystyrene was obtained from Scientific Polymer Products and has $M_n = 98\,000$ and $M_w/M_n = 2.4$. Triphenylsulfonium hexafluoroantimonate(I) was custom-made by Eastman Kodak and phenylbis(*p-tert*-butylphenyl)sulfonium hexafluoroarsenate (II) (Figure 1) was prepared according to the literature.[19] Initiator III is a commercially available product (UVE-1014) obtained from General Electric Co.

Method. Polymer films were prepared by spin coating with a Headway Research Inc. Model EC 101 spin coater. Film thickness was measured with a Taylor-Hobson Tally Step profilometer. Films for deposition studies were cast from 6–8% w/w solutions in cyclohexanone. Film thicknesses were between 0.2 and 1.0 μm. In all cases these films had an optical density of less than 1.0 at 254 nm. The normal onium salt concentration, calculated as the ratio of moles of onium salt to monomer units, was 1:21. UV exposures were performed with a deep-UV light source from Optical Associates Inc. (OAI) equipped with a 500-W mercury–xenon arc lamp and quartz optics. The light was filtered through a 254-nm Hg-line band-pass filter and the dose determined with an OAI Model 355 dose monitor. The flux from the light source was kept at 0.5 mW/s.

A 5-MHz quartz crystal microbalance (QCM) from Sloan Instruments Corp. was used to monitor add-layer formation and polymer deposition rate. All depositions were made at room temperature (21 ± 2 °C) by the following procedure: A polymer/onium salt solution was spin coated on a quartz oscillator crystal. The sample was then exposed to light and transferred to the reaction chamber, which was then evacuated to less than 100 mtorr. The vinyl ether monomer vapor was introduced into the chamber and the temperature, pressure, and deposition of polymer were monitored. The monomer pressure was set with a manual bleed valve. Data were acquired, reduced, and displayed on an IBM PC-XT with a Tecmar Lab Master interface and A/D converter.

ESCA spectra were recorded on a Hewlett-Packard 5950 B ESCA spectrometer equipped with an angular rotation probe. An Al Kα (1486.6 eV) X-ray radiation excitation source was used. Free-standing films (1 μm) for ESCA were prepared on 1-in. Si wafers coated with a 300-Å gold layer. These wafers were then coated with a polymer/onium salt film as described above. The free-standing film was obtained by dipping these wafers into mercury, amalgamating the gold layer, and then removing the films from the mercury bath with tape.

Samples for ^{13}C NMR and GPC analysis were prepared by deposition onto 5-in. Si wafers coated with polystyrene/onium salt II. After reaction, the deposited polymer (poly(vinyl methyl ether)) was rinsed off with methanol, filtered, and concentrated on a rotary evaporator. NMR spectra were recorded in deuteriochloroform on Varian Model EMR-390 and IBM NR/80 spectrometers. GPC measurements were performed on a Waters Model 150 chromatograph equipped with three μ-Styragel columns at 35 °C in tetrahydrofuran.

Results and Discussion

It is somewhat difficult to study the kinetics of surface modification reactions because of the small mass change and the very small thickness changes (typically, less than 1 μm) associated with these systems. Furthermore, one would like to follow the reaction in situ rather than rely on some intermittent measurement technique such as ESCA.

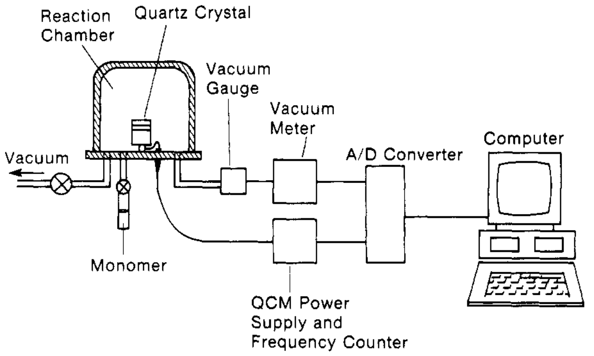

Figure 2. Experimental setup for polymer deposition studies.

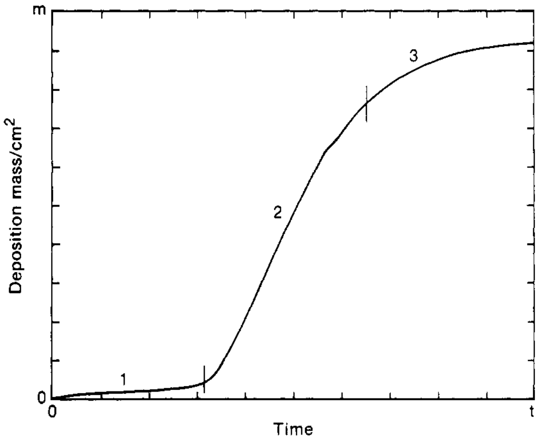

Figure 3. General form of the growth curve for deposition of 2-methoxypropene at 21 °C. The curve is divided into three regions: induction (1), rapid growth (2), and plateau (3).

We have established a very convenient technique for following our reactions in situ through use of a piezoelectric, quartz crystal microbalance (QCM). The characteristic oscillator frequency of the quartz disk in such a device is a function of mass. Hence, the mass of material deposited onto the active area of the crystal can be calculated from an associated frequency shift according to well-established methods.[20]

For a typical AT-cut quartz crystal, the mass sensitivity for a nominal 5-MHz resonator is 5.65 MHz m^2/kg. This means that a frequency shift of 1 Hz corresponds to a mass change of 17.7 ng/cm^2. If the deposited polymer is assumed to have a density of 1 g/cm^3, the deposited thickness corresponding to a 1-Hz frequency shift is 1.8 Å. Such a system can therefore easily follow the deposition process at monolayer resolution. By interfacing the QCM to a computer, for convenient high data rate acquistion of the frequency change, we have created a very sensitive analytical tool for the study of surface modification reactions. An overview of this system is shown in Figure 2.

We have used the QCM in a series of experiments designed to provide information that would lead to a mechanistic hypothesis that is consistent with the observed kinetics. The kinetics can be conveniently divided into three different regions that occur in sequence: induction, rapid growth, and plateau. Figure 3 shows a typical growth curve for these reactions, and the different regions are labeled 1, 2, and 3, respectively.

The observation of an induction period was surprising. If the polymer surface is populated by a strong acid such as $HSbF_6$ following exposure to light, the polymerization should begin the moment that surface is exposed to monomer vapor, not after some delay time. First, we considered the possibility that the surface was contaminated with a base. Atmospheric water, for example, would react

Table I
F_{1s}:C_{1s} Ratio Measured with ESCA for Different Polymer/Onium Salt Combinations

		polymer–air interface	polymer–substrate interface
sample	F:C calcd	F:C found	F:C found
polystyrene/I	0.028	0.000	0.045
polystyrene/II	0.027	0.004	
poly(*p*-methoxystyrene)/I	0.033	0.008	*a*
poly(*p*-methoxystyrene)/I	0.033	0.012	*b*
poly(*p*-methoxystyrene)/II	0.031	0.018	0.048[c]
poly(*p*-methoxystyrene)/II	0.031	0.026	0.048[d]

[a] Baked 15 min at 100 °C. [b] Baked 90 min at 100 °C. [c] Cyclohexane casting solvent. [d] Dimethoxybenzene casting solvent. (Onium salts I and II are shown in Figure 1.)

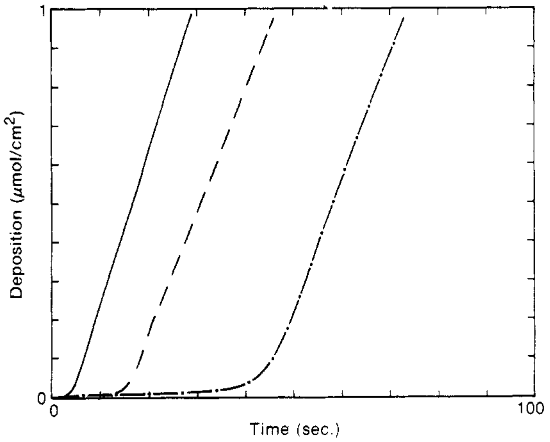

Figure 4. Deposition of 2-methoxypropene on poly(*p*-methoxystyrene)/onium salt I before and after exposure to 100% relative humidity. Monomer pressure, 80 torr; exposure dose, 18.5 mJ/cm^2. (—) Before water treatment; (---) after 2 min at 100% relative humidity; (-·-) after 5 min at 100% relative humidity.

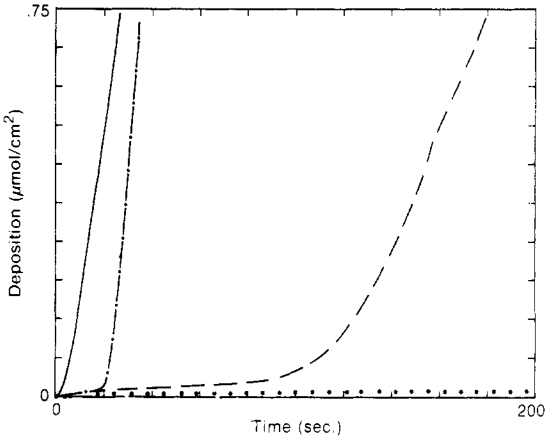

Figure 5. Deposition of 2-methoxypropene onto different polymer/onium salt combinations at 21 °C. Onium salt:monomer unit ratio, 1:21; monomer pressure, 80 torr; exposure dose, 18.5 mJ/cm^2. (—) Poly(*p*-methoxystyrene)/onium salt II; (-·-) poly(*p*-methoxystyrene)/onium salt I; (---) polystyrene/onium salt II; (···) polystyrene/onium salt I.

to form H_3O^+ which is not a strong enough acid to initiate the polymerization. The induction could then result from the time required for *active* initiator to diffuse to the surface, once the source of water was removed.

To test this hypothesis, exposed polymer films containing onium salt were allowed to stand in 100% relative humidity for various times prior to polymer deposition on a QCM. Figure 4 shows the results of these experiments. Increased time of exposure to high humidity does cause a corresponding increase in the induction time, all other factors being constant. Atmospheric moisture does affect the length of the induction period and the water may, in fact, be present as dissolved "water clusters"[21] since the film contains a highly polar onium salt.

Certainly water deactivates the photogenerated acid at the surface of the film and contributes to the induction phenomenon, but water is not the sole contributor. We have found that different polymer–salt combinations have different induction times (Figure 5) even when all of them are treated in exactly the same way. The induction period for films deposited onto polystyrene is always observed to be longer than that for films deposited onto poly(*p*-methoxystyrene). Also, onium salt I always has a longer induction time than onium salt II in the same host polymer. These observations led to an extensive investigation of the surface chemistry of onium salt doped polymer films.

The highly polar onium salts have limited solubility in both nonpolar solvents and lipophilic polymers. It is difficult to mix triphenylsulfonium hexafluoroarsenate with polystyrene, even in low concentrations, without phase separation. However, salts I and II can be incorporated in polystyrene in amounts up to 20 wt %. Even with salts I and II, however, the choice of casting solvent is important and must be a compromise between a polar solvent that is ideal for the salt and a nonpolar solvent that would be ideal for polystyrene. In such a system, the onium salt is more soluble in the moderately polar casting solvent than it is in nonpolar polystyrene. This realization led to the hypothesis that the polymer surface may be depleted in salt concentration relative to the bulk of the film. During the coating process, drying occurs from the air–polymer interface, thereby generating a polymer-rich surface. This concentration gradient could cause the dissolved salt to migrate toward the solvent-rich regions, which are deeper in the film. This migration of salt away from the surface would continue until sufficient solvent (plasticizer) has been removed to raise T_g above ambient temperature. At this point, the diffusion rate would drop, and the resulting concentration gradient would be "frozen in".

If the concentration gradient hypothesis is correct, there should be less than the added amount of onium salt at the film–air interface and more than the added amount at the film–substrate interface. The actual salt concentration at either surface can be calculated from the relative fluorine concentration measured by ESCA. For the front side of the film, this is a straightforward measurement, but for the film–substrate interface the analysis is somewhat more complicated. The main problem is to produce a very thin (1 μm or less) free-standing film after spin coating. This problem was solved by using the "gold-wafer technique" described in the Experimental Section. The ESCA data (Table I) show that there is a significant difference in onium salt concentration between the front side and the back side, supporting the gradient theory.

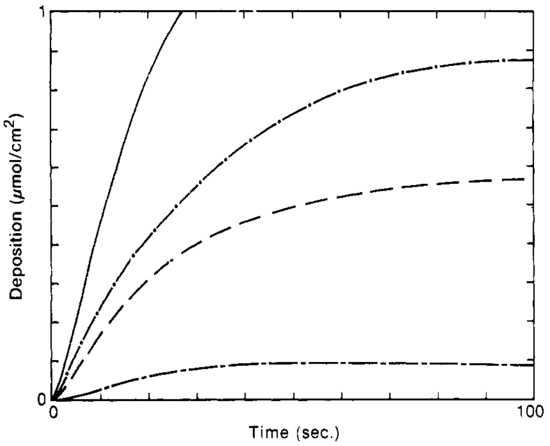

Figure 6. Deposition of 2-methoxypropene onto pure onium salt III, before and after exposure to 100% relative humidity. Exposure doses: (—) 25 mJ cm^2 before water treatment; (-·-) 20 mJ/cm^2 before water treatment; (---) 25 mJ/cm^2, 5 min 100% relative humidity; (--) 20 mJ/cm^2, 5 min 100% relative humidity.

The salt concentrations at the air–film interface follow the solubility characteristics of the salt. The polar salt I suffers greater surface depletion than the less polar di-*tert*-butyl analogue II. Both salts are more soluble in poly(*p*-methoxystyrene) than in polystyrene and both show lower surface depletion in the former polymer than the latter. The concentration variability is consistent with the range of induction times shown in Figure 5. The data in Table I also show that the extent of surface depletion can be altered by adjusting the baking conditions or by varying the casting solvent composition. The salt concentration at the film–substrate interface is higher than calculated for the bulk but does not vary substantially from sample to sample.

The concentration variation, noted in Table I, could represent either a true gradient through the bulk of the film or simply an interfacial phenomenon. Because of the limited penetration depth of ESCA (<50 Å), it is difficult to separate a true gradient from a three-layer stacked distribution. In this three-layer model, a thin layer at the air–film interface is depleted in salt, a thin layer at the substrate–film interface is enriched in salt, and the bulk of the film is of relatively uniform concentration. Argon sputter etch profile and angle-resolved ESCA studies support the three-layer model. The interpretation of these data is complicated, however, because the true Ar etch rate is difficult to measure and the etching process causes chemical transformations in the salts. However, these studies suggest that the depleted salt layer is between 30 and 100 Å thick.

Establishment of this correlation between surface depletion of salt concentration and the duration of the induction time leads to the hypothesis that deposition of monomer onto a film of pure salt should occur without an induction period. Unfortunately, it is somewhat difficult to coat pure films of I or II since they tend to crystallize. However, III, which is a commercially available mixture of onium salts, can be spin coated to form glassy films. Films made from this salt were irradiated and then exposed to 100% relative humidity for various times, followed by monomer deposition in the same way as previously described for the doped polymer films. As shown in Figure 6, no induction period could be measured in these experiments. The only effect of the water treatment was to reduce the overall deposition rate.

The induction phenomenon also shows a strong dependence on the dose used to expose the film (Figure 7). The

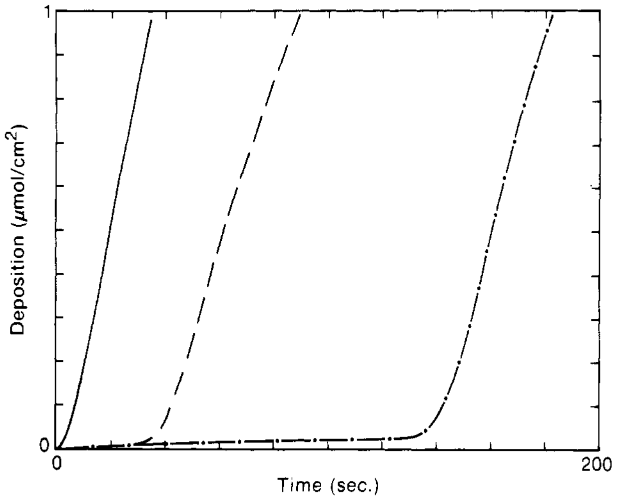

Figure 7. Induction time as a function of irradiation dose for the deposition of 2-methoxypropene onto poly(*p*-methoxystyrene)/onium salt II. Monomer pressure, 80 torr. (—) 18.5 mJ/cm^2; (---) 16.8 mJ/cm^2; (-·-) 13.1 mJ/cm^2.

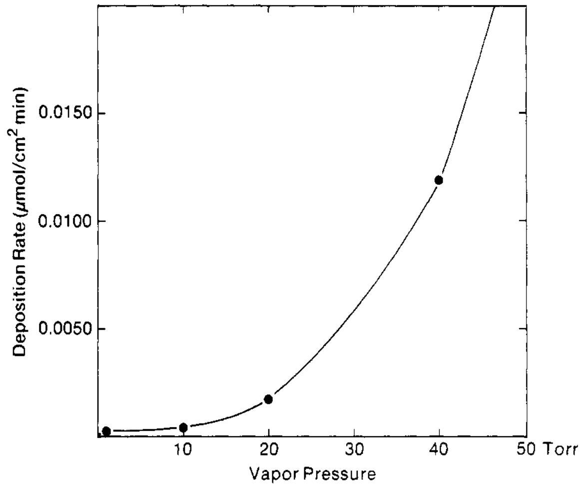

Figure 8. Deposition rate in the linear portion of the growth curve as a function of vapor pressure for the deposition of 2-methoxypropene onto poly(*p*-methoxystyrene)/onium salt II. Onium salt:monomer unit ratio, 1:10.5; exposure dose, 10.2 mJ/cm^2.

quantum yield for the formation of acid from the onium salts is reportedly 0.2–0.4.[22] However, the yield of active catalyst at the surface will be reduced both by reaction with adventitious water and by the low initial salt concentration at the surface.

An understanding of the rapid-growth region of the growth curve and the existence of the plateau phenomenon requires some further mechanistic insight. Interfacial vapor-phase reactions can proceed via one of two fundamentally different mechanisms: a true gas-phase reaction or a surface-phase reaction. The gas-phase reactions are characterized by a linear dependence of deposition rate on gas pressure while the surface-phase reactions show a nonlinear dependence. In this latter process, the reaction takes place in chemisorbed and physisorbed add-layers at the substrate surface rather than directly from the gas phase. A study of the dependence of deposition rate on monomer pressure for the present technique reveals a nonlinear relationship consistent with the surface-phase, add-layer type mechanism. These data are shown in Figure 8.

The realization that the reaction proceeds in an add-layer leads to the question of where initiation actually occurs. There are at least three different possible models

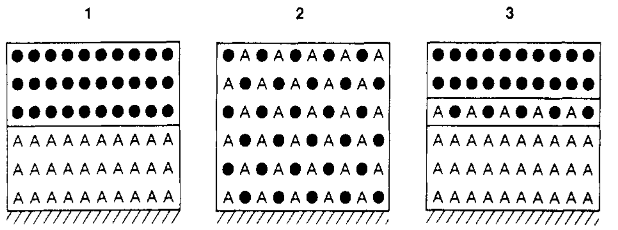

Figure 9. Models for photoinitiated interfacial cationic polymerization. A indicates acidic initiation site, and solid circles indicate monomer.

for the process (Figure 9): (1) the monomer polymerizes at the film–air interface; (2) the monomer diffuses into the host polymer film and polymerization occurs inside the host film surface, forming a polymer blend; or (3) the monomer diffuses into the surface where initiation occurs and then grows out of the interface to form a continuous and homogeneous film.

One way to evaluate these models is to analyze the chemical composition of the surface before any deposition is made, at the onset of the rapid-film growth, and finally after a reasonably thick layer has been deposited. A suitable system for such analysis is the deposition of 2-methoxypropene onto polystyrene/onium salt. In this system, the deposited film of poly(2-methoxypropene) is the only species containing oxygen. Therefore, measuring the C_{1s} and O_{1s} ESCA spectra of samples taken at the three points along the deposition curve makes it possible to determine whether one or both polymers are present at the surface at these points in the deposition process.

The ESCA spectra from such an experiment are shown in Figure 10. The spectrum taken prior to deposition is that of polystyrene and shows only one type of carbon and very little oxygen. A film, quenched at the onset of rapid film growth by pumping out monomer, shows a 1.6-eV shift in the carbon spectrum corresponding to a C–O bond and the appearance of a well-defined oxygen peak. The amount of 2-methoxypropene deposited at this point (Figure 10, point b) was 0.035 μmol/cm^2, which corresponds to a thickness of 150 Å (assuming a density of 1 g/cm^3). If model 1 is correct, this spectrum should be that of pure poly(2-methoxypropene) since the penetration depth of ESCA is considerably less than 100 Å. The calculated carbon:oxygen ratio for this sample is 12:1, and when compared to 4:1 for pure poly(2-methoxypropene) clearly demonstrates that this is a polymer blend. In fact, 12:1 is the theoretical value for a 50:50 blend of polystyrene and poly(2-methoxypropene). In order to fit model 2, this ratio should remain constant as the deposition reaction continues. After deposition of 0.56 μmol/cm^2 (or ~4000 Å) of 2-methoxypropene (Figure 10, point c), the spectra changed completely. The two carbon peaks are now well resolved, the oxygen signal has significantly increased, and the carbon:oxygen ratio has dropped to 5:1, close to the theoretical value for poly(2-methoxypropene). This result is what one expects from model 3. Furthermore, model 3 allows a fairly satisfying explanation for both the induction phenomenon and the rapid film growth.

We believe that according to model 3, the surface of the host film is depleted in salt concentration during the casting process and that most of what salt is present at the surface does not generate initiating species due to reaction of the photogenerated acid with ambient water. However, stable acidic sites do persist just below the surface. When the film is exposed to monomer vapor, an add-layer forms, saturating the surface with monomer. The monomer then diffuses into the film far enough to encounter active initiator and rapid polymerization begins and propagates into the add-layer. The polymerizing surface then has a large number of propagating chain ends ready to react with fresh monomer. Measurement of the counterion (AsF_6^-) concentration at various stages during the deposition lends credence to this model and offers some explanation of the plateau phenomenon.

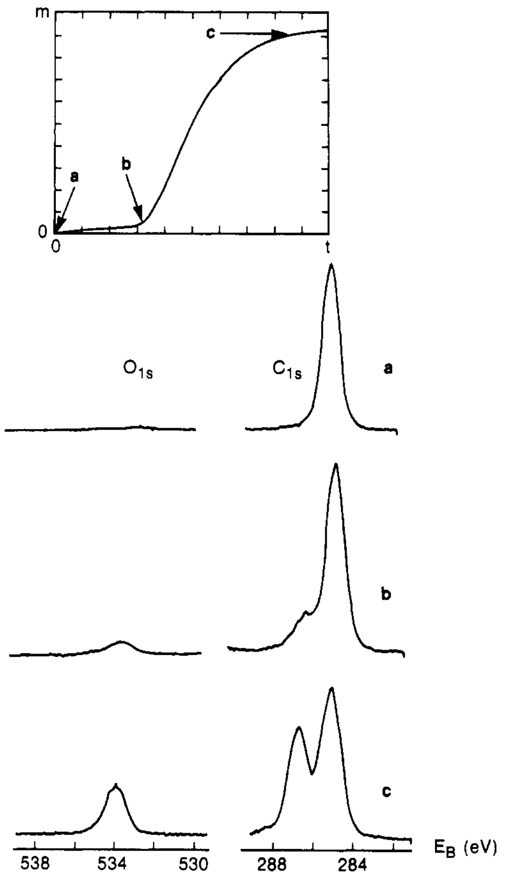

Figure 10. ESCA spectra of a polystyrene/onium salt II surface before, during, and after deposition of 2-methoxypropene. Monomer pressure, 100 torr; exposure dose, 20 mJ/cm^2. Samples taken at points indicated by arrows.

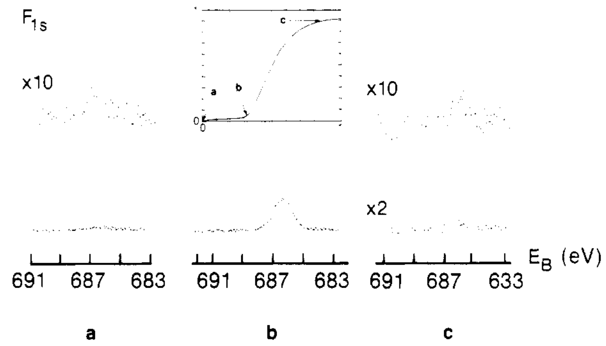

Figure 11. ESCA spectra showing counterion concentration at the surface of a polystyrene/onium salt II film before deposition of 2-methoxypropene, at onset of rapid film growth, and at the plateau where the reaction stops. Monomer pressure, 100 torr; exposure dose, 20 mJ/cm^2.

Measurement of the counterion concentration by ESCA at the onset of rapid film growth (Figure 11, point b) shows a F:C ratio of 0.053, which is *higher* than the theoretical ratio for the bulk sample (F:C = 0.031). As the reaction continues through the period of rapid film growth, there is a gradual decrease in the counterion concentration, perhaps due to trapping of propagating chain ends inside the growing film. At the point of the plateau in growth rate, the concentration of active chain ends (counterion)

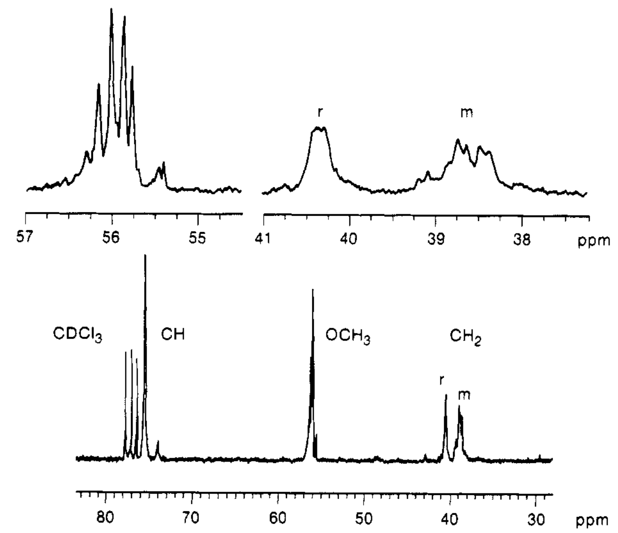

Figure 12. ^{13}C NMR (20 MHz) spectra of poly(vinyl methyl ether) deposited on a polystyrene/onium salt I film. Monomer pressure, 100 torr; exposure dose, 20 mJ/cm^2.

reaches such a low value that growth stops. Surface analysis in this plateau region shows only a very low concentration of counterion (F:C = 0.004). The extent of growth prior to the plateau seems to be a function of the concentration of propagating ends at the onset of rapid growth and the monomer pressure.

Polymers deposited by this surface modification technique were isolated and subjected to analysis. Figure 12 shows the ^{13}C NMR spectrum of poly(vinyl methyl ether) (PVME) polymerized on a polystyrene/onium salt II surface. The spectrum reveals no major side reaction products. The spectra are well enough resolved to allow analysis of tacticity, and the expanded spectra allow analysis of diad, pentad, and hexad sequences. Polymers prepared in this way exhibit a diad ratio M:R = 59:41, which is close to the value observed for PVME polymerized in solution with BF_3 at 0 °C (64:36).[23] The molecular weight of the PVME is rather low, $M_n = 1800$ and $M_w = 4000$, which is expected in view of the high initiator concentration and reaction temperature. The dispersity of the PVME samples is lower than expected (2.2), indicating that chain transfer predominantly occurs to monomer and not to polymer.

Finally, it was observed that the deposition reaction can be terminated during the rapid-growth period by pumping out the monomer and then started again, as long as 2 h later, by introducing new monomer back into the chamber. This pseudoliving characteristic of the system is consistent with the high degree of transfer to monomer.

Conclusion

A novel surface modification technique, photoinitiated interfacial cationic polymerization, is described. This process is characterized by highly nonlinear polymerization kinetics that include an induction period, rapid film growth, and a plateau in growth rate where polymerization stops despite a constant monomer feed concentration. The induction period is related to deactivation of catalyst by water and to a depletion of catalyst in the surface of the host polymer. The initiation occurs some depth into the host polymer and the propagating chain ends migrate through the surface where they encounter available monomer and rapid film growth occurs. The reaction slows and eventually stops because the chain ends are trapped inside the growing film. The properties of the polymers generated in this process are the same as those generated by solution polymerization in terms of stereochemistry, but the molecular weight is fairly low due to the high initiator concentrations that are employed.

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