Polymerization of “Unpolymerizable” Molecules through Topological Control

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Although thermodynamically favorable, polymerization of 1,2-disubstituted ethylenes that contain substituents larger than a methyl group either does not occur or produces only low molecular weight products in low yield following long reaction times.[1−3] The increased steric hindrance between the monomer and growing polymer chain introduces more of a kinetic barrier to the rate of propagation than termination, allowing for only limited amounts of polymer formation.[2,3] For this reason, 1,2-disubstituted ethylenes have historically been referred to as “unpolymerizable” in journal articles,[4−7] textbooks,[2,3] and the common vernacular of polymer chemists. Here, we demonstrate, for the first time, that polymerization of this class of molecules is possible when the steric restrictions are removed by carrying out the polymerizations on ultrathin monomer films that exist in a glassy, isotropic state. Results are presented for three previously non-homopolymerizable 1,2-disubstitued ethylenes: crotononitrile, fumaronitrile, and cinnamyl alcohol.

The deposition−polymerization (DP) technique for the formation of polymer nanofilms is a two-step process. In the first step, a monomer is deposited from the vapor phase onto a substrate cooled well below the freezing point of the monomer. The second step involves exposing the resulting film to UV radiation to initiate polymerization. The separation of these two processes allows for the formation of uniform, defect-free films with thicknesses that can be reproducibly controlled to within several nanometers.[8] We have previously demonstrated the possibility of producing nanofilms of common vinyl polymers such as polystyrene[9] and conducting polymers such as polypyrrole.[10]

Since the monomer is dosed onto a substrate cooled below the monomer freezing point, the resulting film should be in the form of an isotropic glass. This was verified from the infrared spectra of the as-dosed films, which were identical to those obtained from the neat liquid.[9] Since the molecules possess a random distribution of orientations and are effectively locked into place by a lack of translational freedom, it should be possible to polymerize monomers that ordinarily would not polymerize in solution due to steric factors. This novel form of topological[11] control motivated the studies described here.

Molecular films were created by backfilling the desired compound into a vacuum chamber with a base pressure of 10^{-9} Torr. The films were deposited onto a metallic substrate, typically polycrystalline tantalum (although the same results are obtained with a variety of metallic and semiconducting substrates), which was cooled to 100 K. Polymerization was initiated by exposing the films to an unfiltered, broadband HgXe lamp (Oriel Corp.), which provided a power density at the sample surface of 26 mW cm^{-2}. Using this approach, it was possible to reproducibly synthesize films ranging in thickness from several nanometers to several microns, depending on the initial monomer dose.[9] Because of the unique geometry and small size of the samples, a limited number of analytical techniques were available for characterization of both the polymerization process and the final polymer film. Reflection−absorption infrared spectroscopy (RAIRS) was employed for the study of the polymerization process; multiwavelength, single angle ellipsometry was employed to determine film thickness; and temperature-programmed desorption (TPD) was used to verify monomer consumption after polymerization. Additionally, the films were dissolved in an appropriate solvent, and molecular weight analysis was carried out via gel permeation chromatography (GPC) on a system equipped with a single mixed bed column and a refractive index detector.

Fumaronitrile has been shown to photodissociate when exposed to UV radiation.[12] There have also been cases where fumaronitrile was found to polymerize across the nitrile group via anionic polymerization[13,14] as well as radical polymerization,[15,16] but only after several days or weeks and with a final molecular weight of only 1200. The resulting polymer was found to be cyclic and highly conjugated.[16] Generally speaking, fumaronitrile has been considered non-homopolymerizable,[6,7] even though its structure is similar to acrylonitrile, which readily undergoes radical polymerization. Very different behavior was observed when a frozen fumaronitrile film was exposed to UV light. Evidence of isomerization and polymerization occurring simultaneously was found in the IR spectra, as shown in Figure 1. The decrease of the trans out-of-plane (oop) C−H bending and nitrile stretching bands at 975 and 2242 cm^{-1}, respectively, and increase of the cis oop C−H bending and nitrile stretching bands at 760, 2231, and 2260 cm^{-1} indicate that isomerization is occurring. A new band forms at 2260 cm^{-1} and is the only band present in the nitrile stretching region when the polymerized film is heated to room temperature. Further indication of saturation can be seen by the simultaneous decrease of the unsaturated C−H stretching band at 3060 cm^{-1} and increase of the saturated C−H stretching band at 2985 cm^{-1}. This convincing argument, combined with the lack of evidence for the formation of C═N bonds, suggests that polymerization is occurring exclusively across the carbon−carbon double bond. The IR spectrum at room temperature does show evidence of some unsaturated species present in the polymer structure, which could be a result of residual monomer or termination by disproportionation. Finally, it was found that 50% conversion was reached after only 3.5 min.

Similar to fumaronitrile, solution-phase crotononitrile has been seen to mainly undergo isomerization[17,18] and photodissociation[19−21] upon exposure to UV radiation. Despite multiple studies conducted on the photochemistry of crotononitrile, there has been no report of polymerization. During irradiation of a frozen film of crotononitrile, changes in the intensity of IR absorption bands were observed that demonstrate that isomerization is occurring simultaneously with polymerization, as shown in Figure 2. The overall intensity of the C═C vibrational bands decreases upon exposure, indicating saturation of the carbon−carbon double bond. These bands completely disappear when the sample is heated to room temperature after polymerization due to desorption of residual unpolymerized material. The nitrile stretching band at 2224 cm^{-1} decreases in intensity

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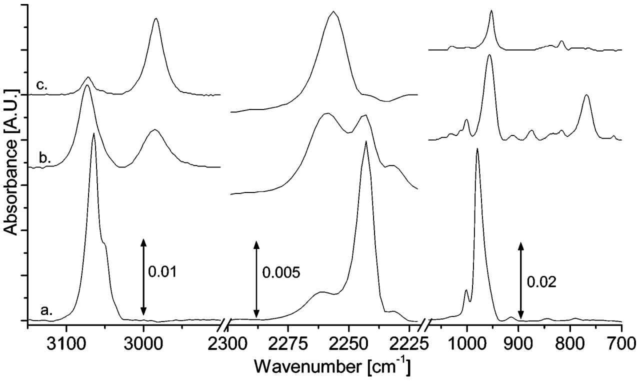

Figure 1. RAIRS spectra acquired during polymerization of fumaronitrile: (a) as-dosed film at 100 K; (b) the same film during UV exposure at 50% conversion; (c) the final polymer film after heating to room temperature.

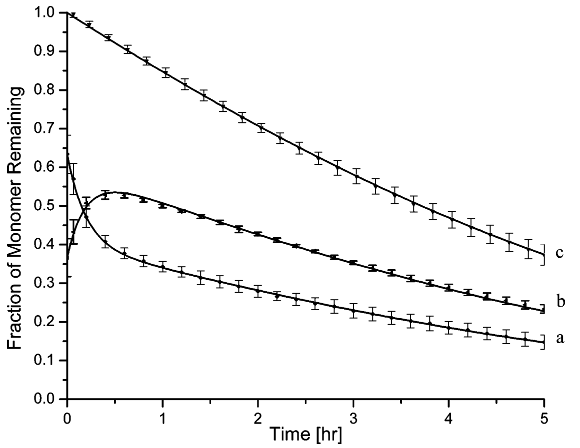

Figure 2. RAIRS results from a crotononitrile film during UV irradiation: (a) trans C=C stretching mode at 1637 cm^{-1}; (b) cis C=C stretching mode at 1628 cm^{-1}; (c) total monomer concentration calculated from the two conformers.

and shifts to 2240 cm^{-1}, which is also attributed to C=C bond saturation. This has been observed previously in the polymerization of acrylonitrile, and further corroboration was provided by carrying out ab initio Hartree−Fock quantum chemical calculations at the 6-31G(d,p) level of theory using Gaussian 03W.[22] Analysis of the vibrational bands resulting from unreacted crotononitrile showed that 50% conversion was reached after 228 min of UV exposure. No evidence was found for the presence of side reactions in either the FTIR spectra acquired during polymerization or the mass spectra acquired as the sample was heated to room temperature. The fact that most of the crotononitrile was consumed during polymerization was additionally verified by postpolymerization TPD.

There is a limited amount of published information on the photochemistry of cinnamyl alcohol.[23] It was found that when irradiated in solution, ∼2% of the cinnamyl alcohol undergoes [2 + 2] cylcoaddition to produce cyclobutane products. Using the DP method, there is clear evidence in the in-situ IR spectra of polymerization through the saturation of the vinyl group. Specifically, all of the vibrational modes associated with the vinyl group decrease upon exposure to UV and disappear completely upon heating to room temperature. The IR spectrum taken at room temperature only contains vibrational modes that correspond to a saturated polymer structure. The polymerization of cinnamyl alcohol occurs very fast, reaching 50% conversion after 2 min.

While infrared spectroscopy provides strong evidence that polymerization is occurring in these systems, it provides no molecular weight information. GPC was therefore employed to determine the molecular weight of the polymer samples. Representative GPC traces from all three polymers produced in this study are shown in Figure 3, and the relevant molecular weight parameters are listed in Table 1. The molecular weight varied slightly as a function of UV intensity and reaction time, but these results are typical of polymers formed via the DP method. From this evidence, it is abundantly clear that high molecular weight polymer is formed. Additionally, the polydispersity index (PDI) of all three polymers represents an upper limit on the actual value, since only a single mixed bed column was employed for separation.

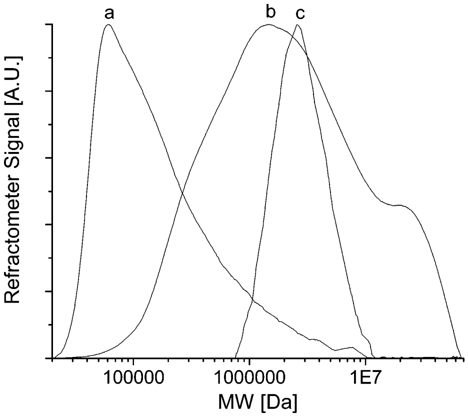

Figure 3. GPC traces from representative samples of polymers produced via the DP method: (a) poly(cinnamyl alcohol), (b) poly(fumaronitrile), and (c) poly(crotononitrile).

Table 1. Summary of the Number-Average (M_n), Weight-Average (M_w), and Polydispersity Index (PDI = M_w/M_n) Values Determined for the Three Polymers in This Study

polymer	M_n	M_w	PDI
poly(fumaronitrile)	1.3×10^6	2.6×10^6	2.0
poly(crotononitrile)	1.6×10^6	2.0×10^6	1.3
poly(cinnamyl alcohol)	5.0×10^5	1.0×10^6	5.0

It should be noted here that it was not possible to generate enough polymer to perform NMR analyses. By taking into consideration the output spectrum of the lamp and the absorptivity of the monomers, it is seen that the UV intensity falls to less than 10% of the incident value at a depth of only 100 nm in the sample film. This places a restriction on the maximum thickness of polymer film that can be formed at several hundred nanometers, which does not result in enough material to perform NMR analyses.

For the first time, photoinduced radical polymerization of three previously non-homopolymerizable molecules was accomplished with short reaction times and high conversions using topological control. However, unlike previously reported topochemical polymerizations, the presence of molecular disorder was the major factor leading to polymerization. While the reduced temperature reduces the number of intermolecular collisions, the disordered nature of the solid film provides a finite probability of adjacent monomers having the proper orientation for polymerization to proceed. The kinetic barrier to polymerization is thereby removed, and high molecular weight polymer can be formed. Thus, these compounds, once relegated to the category of simple molecules, can now be considered viable monomers for the formation of high molecular weight polymers. The extension of this method to a variety of 1,2-disubstituted vinyl monomers, as well as a detailed kinetic analysis of this process, will be detailed in future publications.

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