Synthesis of Cross-Linked Ethylene Glycol Dimethacrylate and Cyclic Methacrylic Anhydride Polymer Structures by Pulsed Plasma Deposition

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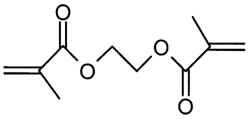
ABSTRACT: New types of reaction pathways have been identified during pulsed plasma polymerization of difunctional precursor molecules. Ethylene glycol dimethacrylate is found to give rise to a highly cross-linked polymeric network, while methacrylic anhydride undergoes cyclopolymerization. The deposited films have been characterized by infrared spectroscopy and solvent swelling studies.

1. Introduction

The quest for retention of precursor functional groups during plasma polymerization has been actively pursued in the past. The very nature of an electrical discharge (ultraviolet photons, electrons, ions, as well as excited neutrals) tends to dissociate the precursor molecule into many fragments to give films which often bear little or no resemblance to the molecular structure of the original monomer.[1−3] The most effective method to date for achieving high structural retention in the final plasma polymer film has been pulsing the electrical discharge on the millisecond−microsecond time scales.[4−8] This comprises the generation of active sites (predominantly radicals) at the surface and in the plasma during the duty cycle on-period, followed by conventional polymerization reaction pathways proceeding during the extinction period. Typical time scales are of the order of microseconds and milliseconds, respectively. Plasma polymer films containing high levels of anhydride,[5] carboxylic acid,[9] cyano,[10] epoxide,[11] hydroxyl,[12] perfluoroalkyl,[13] perfluoromethylene,[4,14] and trifluoromethyl[15] groups have been successfully prepared by this technique.

In this article, the pulsed plasma chemistry of diene monomers is explored with respect to cross-linking and cyclopolymerization reaction pathways. Monomers of this type containing two equivalent polymerizable groups are often employed in solution phase chemistry to make cross-linked polymer networks.[16] One notable exception is 1,6-dienes, which are capable of undergoing cyclopolymerization to give linear polymers via an intramolecular−intermolecular chain propagation mechanism.[17] This latter process is favored due to the intramolecular proximity of the vinyl groups and the strong driving force associated with five- or six-membered ring formation.[18]

Two different length diene monomers have been chosen in the present study to see whether analogous cross-linking and cyclopolymerization reactions can proceed in the proximity of pulsed electrical discharges. First, there is a 1,9-diene, ethylene glycol dimethacrylate, structure **1**, which is often used to make highly cross-linked films imparting good chemical and mechanical stability characteristics.[16] The other monomer is methacrylic anhydride, structure **2**, which is a typical 1,6-diene, renowned for its abilitiy to undergo conventional cyclopolymerization in solution.[17,19] Infrared spectroscopy and swelling studies have been employed to establish whether these monomers follow equivalent cross-linking or cyclopolymerization reaction pathways during exposure to a pulsed electrical discharge.



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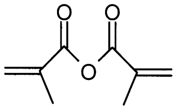

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2. Experimental Section

Plasma polymerization was carried out in a cylindrical glass reactor pumped by a mechanical rotary pump via a liquid nitrogen cold trap (base pressure = 1×10^{-3} mbar, leak rate = 1.2×10^{-9} mol s^{-1}). A copper coil wrapped around the reactor was coupled to a 13.56 MHz radio-frequency power supply in conjunction with an LC matching network. Prior to each experiment, the chamber was cleaned using a 50 W air plasma at 0.2 mbar pressure for 30 min. Monomer vapor (freeze−pump−thawed several times) was then introduced through a fine control needle valve into the chamber for 5 min, followed by plasma ignition. Upon completion of film deposition, the electrical discharge was switched off and the precursor allowed to continue to pass over the substrate for a further 5 min (capping of reactive sites). In the case of pulsed plasma polymerization, a signal generator was used to trigger the rf

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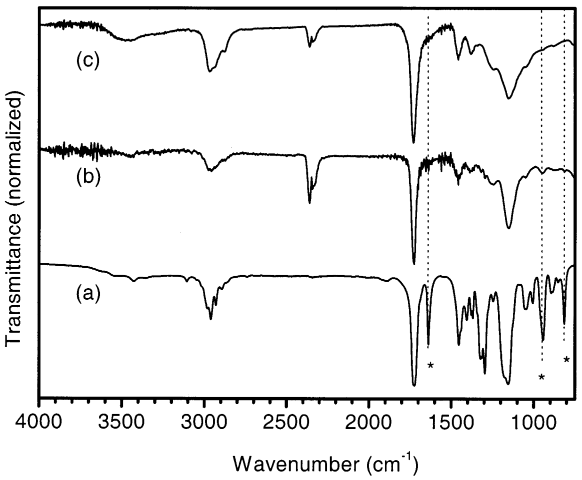


Figure 1. Infrared spectra of (a) ethylene glycol dimethacrylate monomer, (b) pulsed plasma polymer (time on = 20 μs, time off = 20 ms, peak power = 40 W), and (c) 3 W continuous wave plasma polymer. (Asterisk denotes C=C bond features in the monomer, and the weak band in the 2360−2330 cm^{-1} region is due to residual CO_2 in the spectrometer.)

power supply, and the pulse shape was monitored with an oscilloscope.

Plasma polymerization of ethylene glycol dimethacrylate (Aldrich, 99% purity) was carried out at 0.1 mbar pressure for 30 min onto sodium chloride disks and silicon wafers for infrared analysis and thickness measurements, respectively. In the case of methacrylic anhydride (Aldrich, 99% purity), plasma polymer films were deposited onto potassium bromide disks at 0.2 mbar pressure under continuous wave and pulsed plasma conditions for 30 and 120 min, respectively. Different times were employed in order to give equivalent thicknesses, i.e., rule out solvent diffusion effects. Deposition time did not affect film structure.

Infrared spectra of the plasma deposited films were acquired in air using a Perkin-Elmer Spectrum One spectrometer operating in transmittance mode at 4 cm^{-1} resolution and averaged over 32 scans. No aging effects were observed for the plasma polymer layer over a period of 2 months. A reference spectrum of each monomer was obtained by placing a drop of liquid between pairs of either sodium chloride or potassium bromide plates.

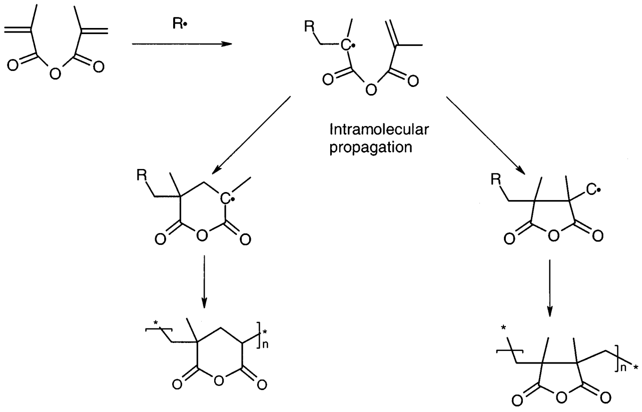
Plasma polymer film thicknesses were measured using a spectrophotometer (Nanoptix NKD 6000). Transmittance−reflectance curves spanning the 350−1000 nm range were fitted with the Cauchy model using a modified Levenburg−Marquardt procedure.

Swelling studies of the cross-linked ethylene glycol dimethacrylate plasma polymer films were carried out by immersing coated silicon substrates into tetrahydrofuran (Rectapur, 99%) for 18 h, followed by measurement of thickness.

3. Results and Discussion

3.1. Ethylene Glycol Dimethacrylate. Infrared band assignments of the monomer were made as follows:[20] unsaturated C−H stretching (3106 and 2981 cm^{-1}), methyl C−H stretching (2960 cm^{-1} antisymmetric, 2929 cm^{-1} symmetric), ethylene C−H stretching (2930 cm^{-1}antisymmetric, 2894 cm^{-1}symmetric), acrylate C=O stretching (1725 cm^{-1}), acrylate C=C stretching (1638 cm^{-1}), CH_3 bending (1453 cm^{-1} antisymmetric and 1368 cm^{-1} symmetric), $=CH_2$ wagging (943 cm^{-1}), and $=CH_2$ twist (814 cm^{-1}) (Figure 1). The pulsed plasma deposited films were found to display all the bands associated with the monomer apart from the carbon−carbon double-bond features (1638, 943, and 814 cm^{-1}). This signifies polymerization of the two methacrylate groups to form a cross-linked network.[16] Furthermore, the C−O stretching band at 1150 cm^{-1} appeared to be far better resolved compared to its continuous wave counterpart (reflecting better structural retention). In fact, the general spectral broadening observed under continuous wave plasma conditions was taken as being indicative of extensive monomer fragmentation and rearrangement.

Scheme 1. Mechanism of Conventional Solution Phase Cyclopolymerization of Methacrylic Anhydride



The degree of cross-linking present in the two types of ethylene glycol dimethacrylate plasma polymer film was compared using solvent swelling experiments. It was found that a 234 ± 3 nm thick pulsed plasma polymer film increased to 258 ± 5 nm upon immersion in tetrahydrofuran, whereas a 180 ± 4 nm thick continuous wave plasma polymer film swelled to 350 ± 5 nm (almost double) under similar conditions. Hence, it would appear that the former contains a far higher level of cross-linking attributable to its better structural integrity. Cross-linking will have taken place by activation and polymerization of the two methacrylate groups contained in the monomer. Further evidence to support this conclusion is provided by taking into consideration that a 220 nm thick conventional solution phase polymerized (cross-linked) poly(ethylene glycol dimethacrylate) film is reported to increase to 280 nm thickness upon soaking in tetrahydrofuran[16] (which is comparable to the behavior observed for the pulsed plasma layer deposited in the present study).

3.2. Methacrylic Anhydride. Methacrylic anhydride is a 1,6-diene molecule which readily undergoes cyclopolymerization in the solution phase. By varying the experimental conditions, it is reported that the ring size can be controlled during homopolymerization. Temperature, solvent polarity, and monomer concentration are considered to be key parameters which govern whether five- or six-membered anhydride ring formation occurs[18,19,21−25] (Scheme 1).

The following infrared band assignments can be made for the methacrylic anhydride precursor molecule:[20] unsaturated C−H stretching (3111 and 2986 cm^{-1}), saturated C−H stretching (2931 and 2963 cm^{-1}), anhydride C=O stretching (1800 cm^{-1}, 1785, 1749, and 1723 cm^{-1}), acrylate C=C stretching (1637 cm^{-1}), $=CH_2$ wagging (948 cm^{-1}), and $=CH_2$ twisting (808 cm^{-1}) (Figure 2).

Pulsed plasma deposited films of methacrylic anhydride were found to display the following bands: C−H stretching (2978, 2936, and 2879 cm^{-1}), anhydride C=O stretching (1858, 1804, 1762, and 1737 cm^{-1}). Some absorbed water was also detected (O−H stretching at

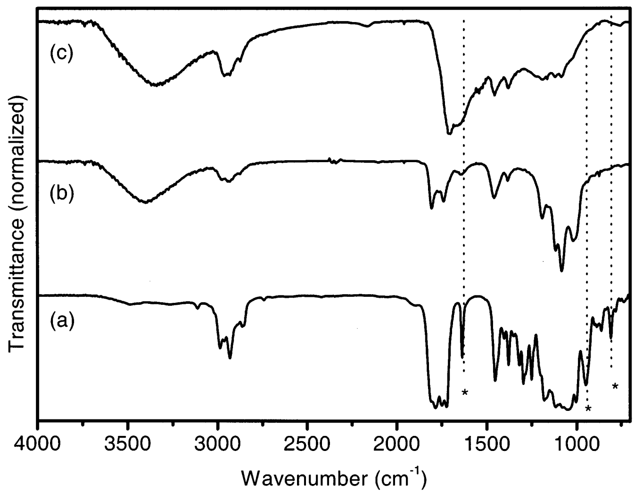


Figure 2. Infrared spectra of (a) methacrylic anhydride monomer, (b) pulsed plasma polymer (time on = 20 μs, time off = 20 ms, peak power = 40 W), and (c) 3 W continuous wave plasma polymer. (Asterisk denotes C=C bond features in the monomer.)

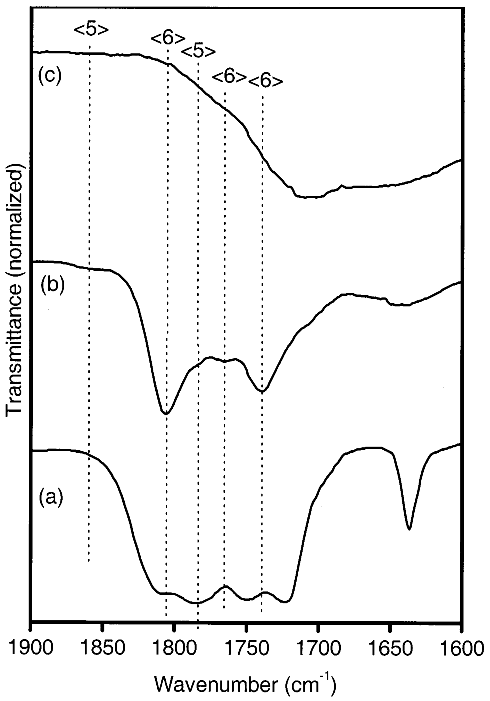


Figure 3. The 1900−1600 cm^{-1} infrared absorption region of (a) methacrylic anhydride monomer, (b) pulsed plasma polymer (time on = 20 μs, time off = 20 ms, peak power = 40 W), and (c) 3 W continuous wave plasma polymer. (The numbers denote the assigned ring size.)

3397 cm^{-1} and O−H bending at 1641 cm^{-1}). The exact position of the C=O stretching bands associated with the anhydride group acts as a fingerprint region to help distinguish between linear and cyclic anhydrides as well as the actual ring size[20] (Figure 3). It is reported that linear anhydride C=O stretching absorbances should appear at 1827 and 1766 cm^{-1}.[20] However, these are not observed. Instead, peaks at 1805, 1765, and 1740 cm^{-1} were identified, which are indicative of C=O stretching features belonging to six-membered poly(methacrylic anhydride) rings.[19] The multiple peaks stem from different stereoisomers.[2] Also, the very weak C=O stretching absorbances at 1860 and 1780 cm^{-1} suggest the presence of a minor constituent of five-membered poly(methacrylic anhydride) rings present in the overall polymer structure.[20] The high selectivity toward six-membered ring formation in the case of pulsed plasma polymerization of methacrylate anhydride can be attributed the greater stability of the tertiary radical intermediate formed in this case compared to the primary radical intermediate required for five-membered ring cyclopolymerization (Scheme 1).

Continuous wave plasma polymer deposition gave rise to poorly resolved peaks (e.g., 1000−1250 cm^{-1}) as well as only one broad peak at 1710 cm^{-1} in the 1800−1700 cm^{-1} region. These features implicate the destruction of the anhydride functionality contained in the precursor molecule during continuous wave conditions.

4. Conclusions

In the case of difunctional monomers, two alternative reaction pathways have been identified during pulsed plasma polymerization. Ethylene glycol dimethacrylate (a 1,9-diene) leads to the formation of a cross-linked polymer network, while methacrylic anhydride (a 1,6-diene) undergoes homocyclopolymerization. This is in marked contrast to continuous wave plasma conditions, where for both precursors the more energetic environment gives rise to poor overall reaction selectivity.

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