

Advanced Dielectrics for Microelectronics: Chemically Amplified, Low- κ Materials

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Abstract and Introduction:

Shrinking of the microelectronics package requires advanced low dielectric constant (low- κ) materials. Organic polymers offer more environmentally friendly and moldable options than inorganic materials.

In organic polymers, photo-definable dielectrics can be directly patterned by photolithographic means [1]. Lithographically printed dielectrics do not require the use of photoresist or additional pattern transfer steps, which can be costly and expose the device to aggressive wet or dry etch process steps. Some organic, photo-definable polymers can be catalytically depolymerized by a small light stimulus.

The catalytic phenomenon is called chemical amplification, and the polymers that depolymerize completely are called self-immolative polymers (SIPs) [2]. Photo-definable SIPs are depolymerized and become monomers through the light stimulus. Here, if vapor pressure of the monomer is high, the exposed material can evaporate and disappear completely, which can skip the developing steps in traditional processing because only light exposure and dry developing are needed. However, a conventional photo-definable SIP such as polyphthalaldehyde [3] has inherent problems, for example, low mechanical strength and low vapor pressure of monomers.

Low mechanical strength makes them difficult to use as an interlayer insulating film, and low vapor pressure increases dry develop time.

In this report, the preparation method of copolymers that have high mechanical strength and higher vapor pressure is discussed. In order to obtain the ideal copolymer, butyraldehyde (BA) or pivalaldehyde (PVA) are used as a monomer with PHA. BA and PVA has high vapor pressure and their polymers are expected to have high mechanical strength because of their high crystallinity.

Experimental:

Figure 1 shows the monomers used in this research. Copolymers were synthesized by following a paper that describes the anionic polymerization of polyphthalaldehyde [4]. Scheme 1 shows the synthesis procedure of copolymers. PHA (1.0 equiv), BA or PVA (0.25 equiv), and *N*-hydroxysuccinimide in THF (0.01 M, 0.00024 equiv) were added to a vial in a glovebox under an argon atmosphere. THF was added to create a 1.0 M aldehyde solution. The reaction mixture was cooled to -70°C .

After 30 min, a solution of 1-*tert*-butyl-2,2,4,4,4-pentakis(dimethylamino)- $2\lambda^5,4\lambda^5$ -catenadi-(phosphazene) (P2-*t*-Bu base) in THF (2.0 M, 0.0048 equiv) was added to the solution, and the reaction mixture was stirred at -70°C . After two hours, the polymer was end-capped via sequential addition of pyridine (0.6 equiv) and methylchloroformate (0.04 equiv) to the -70°C solution. The solution was allowed to warm to room

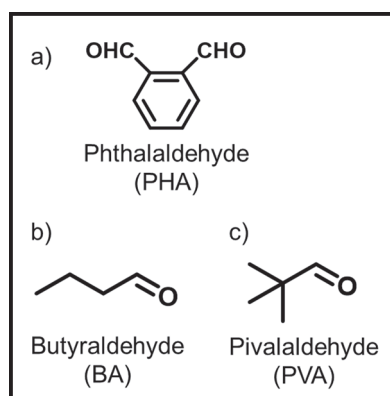
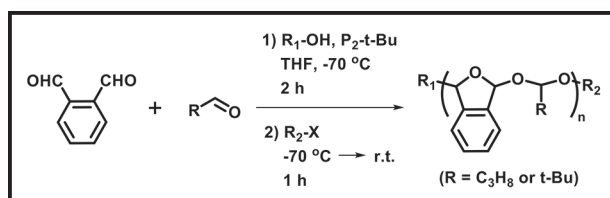


Figure 1: Chemical structures of a) phthalaldehyde (PHA), b) butyraldehyde (BA), and c) pivalaldehyde (PVA).



Scheme 1: Synthesis procedure of copolymer.

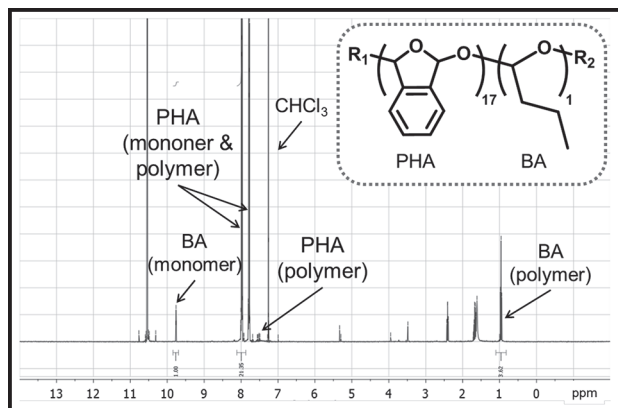


Figure 2: ^1H NMR spectrum of PHA-BA copolymer.

temperature an hour later. The polymer was precipitated by adding the reaction mixture to a solution of 200 mL cold methanol. The resulting suspension was filtered, and the precipitate was washed using methanol. The resulting polymer was dried overnight.

The yields of the PHA-BA and PHA-PVA copolymers were 42 wt% and 20 wt%, respectively.

Results and Discussion:

Figure 2 shows ^1H NMR spectrum of the copolymer, which suggests the mole ratio of PHA to BA is 17 to 1. It suggests the synthesis did not go as expected because the mole ratio was initially 4 to 1. One possible explanation is the acidic α -hydrogens of BA caused a side reaction with the anionic propagation that impeded the polymerization. A copolymer of PHA and PVA was then tried, which has no α -hydrogens to interrupt the polymerization. Figure 3 shows ^1H NMR spectrum of the PHA-PVA copolymer, which suggests the ratio of PHA to PVA is 76 to 1. This means almost all of the monomers in the polymer chain are PHA, which is not desired. The low PVA content is probably due to the methyl groups of PVA having high steric hindrance. A new monomer whose methyl groups are substituted for less bulky groups such as fluorine should be used in the future.

Conclusions and Future Work:

A PHA-BA copolymer was synthesized with the goal of obtaining a copolymer with high mechanical strength and high vapor pressure of the monomers. ^1H NMR of the

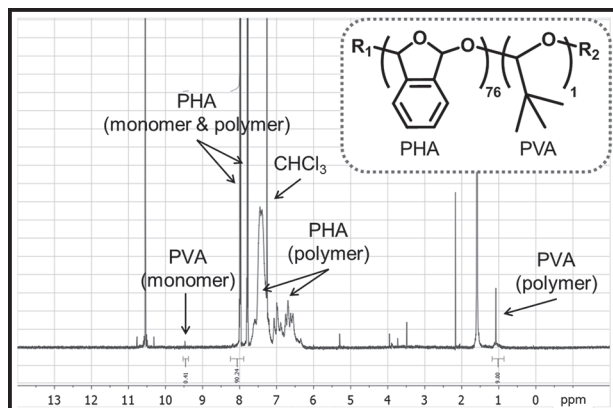


Figure 3: ^1H NMR spectrum of PHA-PVA copolymer.

copolymer shows the mole ratio of PHA to BA is 17 to 1, which does not substantially improve the monomer vapor pressure after depolymerization as desired. The differences between expected and actual copolymer content is likely due to the α -hydrogens of BA. A PHA-PVA copolymer, which has no α -hydrogens, was attempted, but ^1H NMR showed only small amounts of PVA were polymerized. The bulky methyl groups of PVA likely prevented incorporation into the polymer chain. A less bulky monomer that has no α -hydrogens, like 2,2,2-trifluoroacetaldehyde, will be investigated in the future.

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