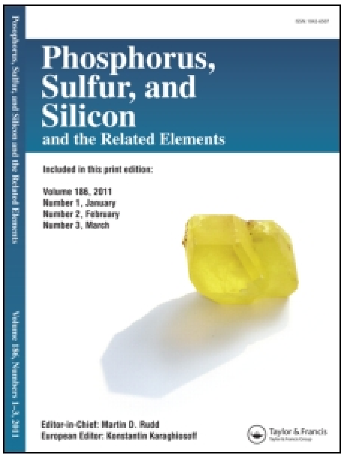

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Manufacture of Vinylidene Diphosphonic Acid and Novel Phosphorus-Containing Polymers

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MANUFACTURE OF VINYLIDENE DIPHOSPHONIC ACID AND NOVEL PHOSPHORUS-CONTAINING POLYMERS

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A novel method for the preparation of vinylidene diphosphonic acid (VDPA) is described. Incorporation of this monomer into water-soluble polymers is discussed.

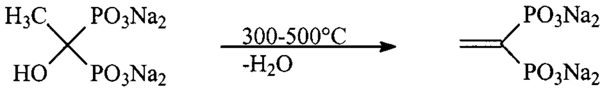
Keywords: Applications; polymers; Rhodia; synthesis; vinylidene diphosphonic acid

Vinyl phosphonic acid (VPA) is used as a monomer in polymer synthesis, and due to the interesting profile of properties, polymers containing VPA are widely used in a diverse range of applications. For example, they have been patented for use in dental care products, ink concentrates, and flame retardants, to name but a few. By analogy, vinylidene diphosphonic acid (VDPA) may be expected to have similar or superior properties in certain applications by virtue of its higher phosphorus content and charge density.

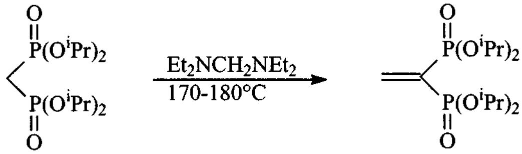
VDPA is known for its use as a chelant[1] for metals and for use in certain pharmaceutical applications.[2] VDPA and VPA may be used in combination with each other and other polymerizable monomers, depending on the required properties and the specific application. However, unlike VPA, VDPA is not readily available commercially. We now report[3] that VDPA may be prepared by a facile method that produces VDPA in a stable, pure form, in high yield, and requiring minimal purification from the salt of α-hydroxy-ethyl diphosphonic acid dimer (ADPA dimer) by the low-temperature thermolysis of the reactant followed by acidification. Also, we report the incorporation of VDPA and VPA as an end group[4] into novel water-soluble polymers.

METHODS OF PREPARATION

VDPA is conventionally prepared from either methylene bisphosphonates,[5]



or from diphosphonic acid derivatives:[6]



There are several disadvantages associated with the known methods of preparation, although not all disadvantages may be associated with each method.

Some require high dehydration temperatures, typically >400°C, to produce VDPA. This is above the decomposition temperature of ~285°C of tetrasodium VDPA and hence products are obtained in low yield (50–75%) and are of relatively low purity (up to 80 mol%) due to the presence of large amounts of esters. This may be unacceptably low for some uses, for example, pharmaceutical applications. Additionally, products typically obtained by these methods require cumbersome purification methods, which are less commercially viable.

RHODIA'S MANUFACTURING ROUTE

We have discovered that VDPA may be conveniently prepared from the salts of ADPA dimer hydrate. This requires the dehydration of the reactant followed by a low temperature pyrolysis as shown in Figure 1.

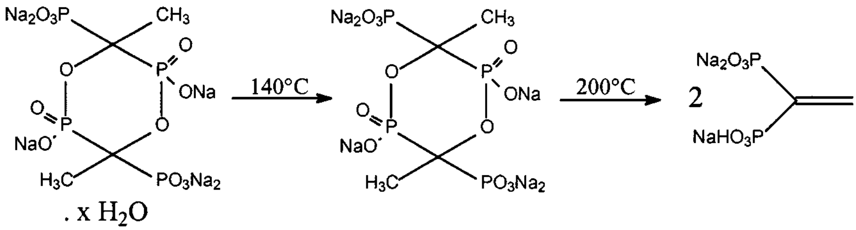


FIGURE 1

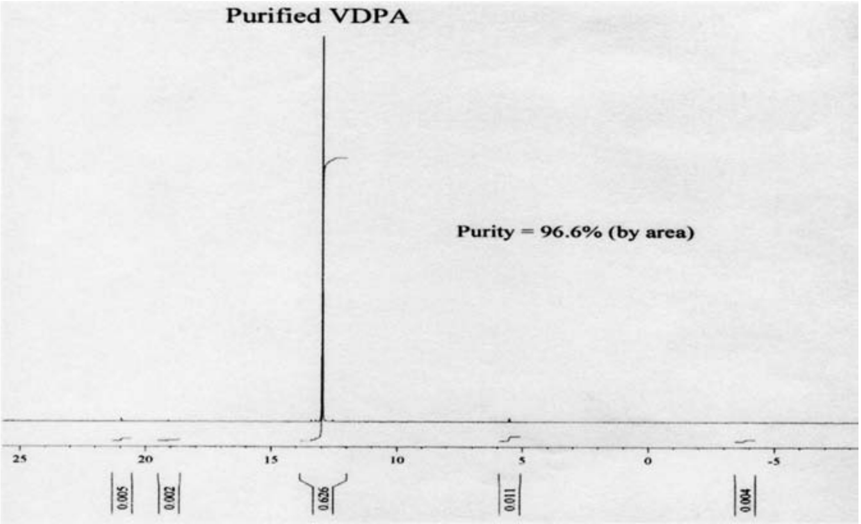


FIGURE 2

The product is isolated as the tetrasodium salt (after neutralization) and is usually obtained as a white or off-white crystalline solid. Yields of at least 80% are obtained and the product is typically >95 mol% pure (see NMR spectrum in Figure 2).

NOVEL "END-CAPPED" POLYMERS

VDPA is a versatile monomer offering potential for use in many applications. Our studies show that polymers incorporating VDPA have yielded polymers with unique and interesting properties.

Initial attempts to copolymerize VDPA with other monomers such as acrylic acid, vinyl sulfonic acid, and others met with limited success. This has been attributed to the high steric requirements of VDPA and apparent low reactivity leading to low-molecular-weight copolymers. We have had more success with the incorporation of VDPA at the end of the polymer chain, giving rise to "end-capped" polymers.

As already mentioned, the "end cap" confers unique properties on the polymer such as metal chelation and increased thermal stability. Reaction of VDPA with sodium hypophosphite yields tetrasodium 1,1-diphosphono-2-phosphinoethane (DPPE).

DPPE is a useful intermediate, which can be further reacted with other monomers to give rise to "end-capped" phosphonate polymers as in Figure 3.

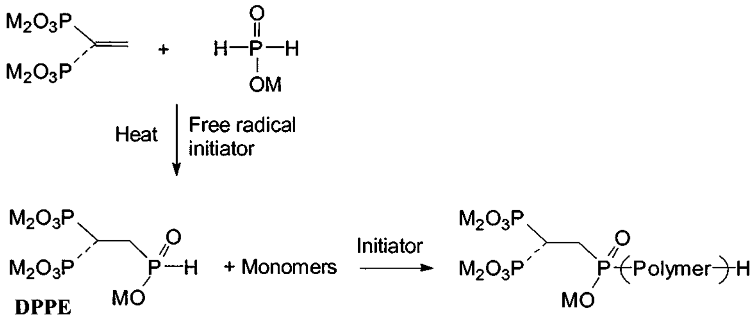


FIGURE 3

PROPERTIES

VDPA- and VPA-end-capped polyacrylic acid polymers have been found to have superior thermal stability at elevated temperatures up to 180°C when compared with conventional copolymers of VPA with water-soluble monomers such as acylic acid. This was demonstrated by comparing the performance of such compounds as scale inhibitors before and after storage for 5 days at 180°C.

Furthermore, the end-capped polymers show unexpectedly improved adsorption onto minerals such as silica sand. The good adsorption/metal-chelating properties of the end-capped polymers combined with their water solubility make polymers of this type of interest in a range of applications. The choice of monomer/monomers to be polymerized with the "end caps" can be carefully selected to tune the properties to target specific applications.

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