

Viologen Polymers and Their Application as Functional Materials

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Editorial

The 1,1'-dialkyl-4,4'-bipyridinium salts are commonly called viologens. They are an interesting class of dicationic salts that find many applications in modern science and technology including electrochromic devices, molecular machines and organic batteries [1]. The viologen moieties impart a suite of properties including redox properties, ionic conductivities, thermochromism, photochromism, electrochromism and piezochromism that are the principal reasons for their versatile applications. They are used for the preparation of ionic liquids after suitable chemical modifications of these moieties of varied chemical architectures with the variation of numerous anions. These moieties even form ionic liquid crystals (ILCs) of suitable chemical architectures in combination of appropriate anions. Recently, ILCs is an active area of research in energy-related systems including batteries and dye-sensitized solar cells to combat the global energy crisis. These salts are typically synthesized by the quaternization of 4,4'-bipyridine with alkyl halides or alkyl tosylates i.e., the so called Menshutkin reaction.

Metathesis reactions or anion exchange reactions can then be conducted to common halides or tosylates to triflimide ($-N(Tf)_2$), hexafluorophosphate (PF_6^-), tetrafluoroborate (BF_4^-), triflate (OTf^-) and perchlorate (ClO_4^-), among other anions. They can be incorporated into the polymer chains either in main chain or in the side

chain resulting in viologen polymers using the polymerization reactions known in polymer chemistry. They are also known as ionene polymers or cationic polyelectrolytes because of the presence of cationic nitrogen atoms in the polymer chains. These ionic polymers different from neutral polymers exhibit polyelectrolyte behavior i.e., their inherent viscosities decrease with increasing polymer concentrations in water and organic solvents. Viologen polymers typically are prepared by Menshutkin reaction in polar aprotic solvents such as N,N-dimethylformamide (DMF) and acetonitrile followed by anion exchange reactions of different ions to tune the desirable properties including solubility in different organic solvents and thermal properties. Polymers of various chemical architectures of viologen moieties can also be prepared by ring transmutation reactions of bispyrylium salts with various aliphatic diamines and aromatic diamines in polar aprotic solvent such as dimethyl sulfoxide (DMSO).

They can also be prepared from the reactions of Zincke salts with aromatic diamines. Viologen polymers (main-chain) with halides as counterions generally do not exhibit thermotropic liquid-crystalline (LC) properties, since they decompose before melting transitions because of strong ionic interactions of halide ions with positively charged nitrogen atoms. Additionally, halide ions cause the so called Hofmann elimination at high temperatures to

de-quaternization reactions—the reverse process of polymerization reactions thus causing decomposition. However, this class polymers, after suitably modified chemical architectures with appropriate bulky organic anions such as tosylate and triflimide anions, exhibit thermotropic (heat-induced) LC properties. They show crystal-to-LC (smectic) transitions, T_{ms}, and LC-to-isotropic transitions, T_{is}. Generally, polymers with triflimide anions have lower T_{ms} and T_{is}, but higher thermal stabilities than those with tosylates.

The bulky organic counterions have the unique capacity to reduce the strong ionic interactions that are conducive to lower the T_{ms} and T_{is}. These ions also have low tendency to cause de-quaternization reactions. Interestingly enough, polymers with tosylate as counterions also exhibit lyotropic (solvent-induced) LC phases at room temperature in methanol, ethanol, diethylene glycol, glycerine and benzyl alcohol. Their critical concentrations (C*_s) are as low as 5 wt% and as high as 20-40 wt% in various alcohols depending on the polarity of the solvents, the hydrophilicity and hydrophobicity of the solvents, and the microstructures of polymers. Polymers with triflimide as counterions also exhibit lyotropic LC phase at room temperature in methanol, acetonitrile, DMF and DMSO.

Their C* are 1-5 wt% in methanol and those are 20-70 wt% in polar aprotic solvents. Thus, viologen moieties act as LC forming units for both the thermotropic and lyotropic polymers. They are versatile polymers that have many potential applications. Some of these key applications include as follows. These polymers have the potential for generating electricity from carbohydrates via the viologen-catalyzed alkaline carbohydrate fuel cells wherein these polymers rapidly cause oxidation of carbohydrates to carbonates and water [2]. Viologen polymers (side-chain) are also used in aqueous and nonaqueous media as redox active polymers for energy storage in redox flow batteries that is an area of active research to combat the global energy crisis [3,4].

In addition to main-chain and side-chain polymers, they are incorporated into more complex polymer structures including porous covalent organic frameworks (COFs) that have a number of diverse applications including gas adsorption, organic and inorganic pollutant removal, and sensing and film fabrication [5]. The phenylated poly(pyridinium salt)s are also a class of ionic main-chain polymers (extended viologen polymers) that are usually prepared by the ring-transmutation polymerization reaction of bispyrylium salts and diamines and metathesis reactions [6]. Depending on the chemical

structures of bispyrylium salts and diamines, they can be π -conjugated or non-conjugated ionic polymers.

For example, some non-conjugated ionic polymers exhibit thermotropic LC properties and light-emitting properties in both solution and solid state; others exhibit amphotropic LC properties and light-emitting properties in both solution and solid state. Additionally, π -conjugated and even non-conjugated ionic polymers exhibit lyotropic LC phase in both protic and aprotic solvents and light-emitting properties in both solution and solid state depending on their chemical microstructures. They can be appropriately called as functional ionic polymers. For example, one such poly(pyridinium salt)s prepared from calix[4]arene diamine shows an interesting result that the *Pseudomonas fluorescens* DNA has a strong interaction with this polymer predominantly by electrostatic interactions for sensing as evaluated by fluorescent titration and transmission electron microscopy studies.

Another polymer prepared from benzidine giving rise to conjugated polyelectrolyte that is used to develop a sensitive fluorescence-based biosensor for homogeneous DNA detection. Even a conjugated poly(pyridinium salt)s based on 3,6-diamino-N-butylcarbazole exhibits aggregation-induced light emission property. A fluorescence turn-on biosensor for calf thymus DNA detection and quantification is developed on the basis of this interesting property. Additionally, the dispersion of single-walled carbon nanotubes with poly(pyridinium salt)s via non-covalent interactions in DMSO is achieved for the preparation carbon nanotube based composites. Finally, they are suitable components for the construction of multilayer assemblies with various anionic polymers by the sequential layer-by-layer deposition techniques through electrostatic interactions. These techniques have received significant interest globally to create numerous functional materials.

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