Polyelectrolytes for Thin Film Deposition in Nonlinear Optical and Other Devices

Polyelectrolytes are defined as materials for which the solution properties in solvents of high dielectric constant are governed by electrostatic interactions over distances larger than typical molecular dimensions.[1] These materials are widely used in industrial applications as dispersants in aqueous media, flocculating agents to coagulate slurries and industrial wastes, for sizing in textile and paper manufacture, and as conditioning additives to drilling muds and soil to prevent abrasive damage. More recently, they have been applied in molecular self-assembly techniques for thin film deposition of electrically conducting polymers,[2] conjugated polymers for light emitting devices,[3] nanoparticles,[4] and noncentrosymmetric-ordered second order nonlinear optical (NLO) devices.[5]

A primary requirement for a material to exhibit nonlinear optical activity is that it should be noncentrosymmetric. In polymer-based nonlinear optical materials, the chromophore can be incorporated into a polymer matrix in a number of ways: the guest-host model and various covalent bonding schemes.[6-8] More recently, the electrostatic self-assembled monolayer (ESAM) technique for fabricating noncentrosymmetric structures resulting in a large second order NLO response is being increasingly researched.[5,9,10] The advantages of this technique include long-term stability of $\chi^{(2)}$ in contrast to electric field poling of a glassy polymer, thicker (tens of microns thick) films than by the Langmuir-Blodgett technique, and easier fabrication than by covalent self-assembly methods. By ESAM processing, a multilayer film is formed by alternately immersing the substrate in aqueous solutions of a polyanion and a polycation. Either one or both the polyanion and polycation may contain polarizable chromophores, i.e., be the active polyelectrolyte. In concert with the other variables, the choice of polyelectrolyte can have a marked effect on reinforcing or disrupting the orientation of chromophores in successive layers and, hence, on the second order NLO response.

A sampling of **polyelectrolytes** available from Aldrich is provided below. We also offer an extensive selection of nonlinear optical chromophores, many of which are manufactured in our production plants. As you continue to search for fast and efficient second and third order nonlinear materials, look to Aldrich for your chemical needs. Our product database on the Web, **www.sigma-aldrich.com**, is searchable in eight different ways. If we do not offer the component or composite material you are looking for, please contact us at **aldrich@sial.com**; our R&D team would be glad to consider your needs as a custom project.

Polyelectrolyte	Cat. No.	$\overline{M}_w$/Viscosity	Form	Unit Sizes
Candidates for polycation solutions				
Poly(allylamine hydrochloride); $[-CH_2CH(CH_2NH_2 \bullet HCl)-]_n$				
	28,321-5	15,000	Powder	**5g; 25g**
	28,322-3	70,000	Needles	**1g; 5g; 25g**
Poly(diallyldimethylammonium chloride)				
	52,237-6	5,000–20,000	40 wt. % solution in water	**25mL; 1L**
	Also available in the following molecular weights: 100,000–200,000; 200,000–350,000; 400,000–500,000.			
Poly(acrylamide-co-diallyldimethylammonium chloride)				
	40,908-1	9,000–25,000 cps	10 wt. % solution in water	**1L; 4L**
Candidates for polyanion solutions				
Poly(anetholesulfonic acid, sodium salt)				
	44,446-4	—	Powder	**5g; 25g**
Poly(acrylic acid, sodium salt); $[-CH_2CH(CO_2Na)-]_n$				
	41,601-0	1,200	45 wt. % solution in water	**100mL; 500mL**
	Also available in the following molecular weights: 2,100; 5,100; 8,000; 15,000; 30,000.			
Poly(styrene-alt-maleic acid, sodium salt); $[-CH_2CH(C_6H_5)CH(CO_2R)CH(CO_2R)-]_n$, R = H or Na				
	43,529-5	1,060 cps	30 wt. % solution in water	**250mL; 1L**
Poly(vinyl sulfate, potassium salt); $[-CH_2CH(OSO_3K)-]_n$				
	27,196-9	170,000	Powder	**1g; 5g**
Poly(vinylsulfonic acid, sodium salt), tech.; $[-CH_2CH(SO_3Na)-]_n$				
	27,842-4	4,000-6,000	25 wt. % solution in water	**5mL; 250mL; 1L**

References: (1) For a discussion of the differences between polyelectrolytes and ionomers, see: (a) Eisenberg, A.; Kim, J-S. *Introduction to Ionomers*; John Wiley: New York, NY 1998 (Aldrich Catalog No. **Z41,033-0**). (b) *Specialty Polymers*; Dyson, R.W., Ed.; Chapman and Hall: New York, NY 1987; p 110 (Aldrich Catalog No. **Z22,414-6**). (2) Sayre, C.N.; Collard, D.M. *J. Mater. Chem*. **1997**, *7*, 909. (3) Cheung, J. et al. *Polym. Prepr*. **1993**, *34*, 757. (4) Schmitt, J. et al. *Adv. Mater*. **1997**, *9*, 61. (5) Wang, X. et al. *Macromol. Rapid Commun*. **1997**, *18*, 451. (6) Moerner, W.E.; Silence, S.M. *Chem. Rev*. **1994**, *94*, 127. (7) *Chemistry of Advanced Materials: An Overview*; Interrante, L.V., Hampden-Smith, M.J., Eds.; Wiley-VCH: New York, NY, 1998; p 207 (Aldrich Catalog No. **Z40,863-8**). (8) Prasad, P.N.; Williams, D.J. *Introduction to Nonlinear Optical Effects in Molecules & Polymers*; John Wiley & Sons: New York, NY, 1991 (Aldrich Catalog No. **Z22,382-4**). (9) Roberts, M.J. *Mat. Res. Soc. Symp. Proc*. **1999**, *561*, 33. (10) Liu, Y. et al. *ibid*. **1999**, *561*, 29.

ALDRICH® *chemists helping chemists in research and industry*

P.O. Box 355, Milwaukee, WI 53201 USA **Telephone:** 414-273-3850 • 800-558-9160 **Fax:** 414-273-4979 • 800-962-9591 **Web Site:** www.sigma-aldrich.com

Aldrich is a member of the Sigma-Aldrich family.