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TECHNICAL DATA SHEET

TDS-222
Edition: October 15, 2007
Previous Edition: January, 2002

Molecular Weight of Carbopol®* and Pemulen®* Polymers

Physical and Chemical Properties of Carbopol® and Pemulen® Polymers

Carbopol®-type polymers, such as Carbopol®, Pemulen® and Noveon®, are polymers of acrylic acid, crosslinked with polyalkenyl ethers or divinyl glycol. Carbopol®-type polymers are flocculated powders of particles averaging about 0.2 micron in diameter. The flocculated powders average 2 to 7 microns as determined by Coulter Counter. These agglomerates cannot be broken down into the primary particle once produced.

Each particle can be viewed as a network structure of polymer chains interconnected by crosslinks. Without the crosslinks, the primary particle would be a collection of linear polymer chains, intertwined but not chemically bonded. These linear polymers are soluble in a polar solvent, such as water. Carbopol® 907 is a linear polymer and is soluble in water. All other Carbopol® polymers, Pemulen®, and Noveon® polymers are crosslinked, and swell in water up to 1000 times their original volume (and ten times their original diameter) to form a gel when exposed to a pH environment above 4-6. Since the pKa of these polymers is 6±0.5, the carboxylate groups on the polymer backbone ionize, resulting in repulsion between the negative particles, which adds to the swelling of the polymer. Crosslinked polymers *do not* dissolve in water.

The glass transition temperature of Carbopol®-type polymer is 105ºC in powder form. However, the glass transition temperature drops dramatically as the polymer comes into contact with water. The polymer chains start gyrating, and the radius of gyration becomes bigger and bigger. Macroscopically, this phenomenon manifests itself as swelling.

Defining Molecular Weight for a Polymer

Polymers are heterogeneous mixtures of polymer homologues. When the molecular weight of a polymer is discussed, generally what is being referred to is actually the *average* molecular weight of these homologues. The molecular weight of a polymer is more fully characterized by number average molecular weight (Mn), weight average molecular weight (Mw), and viscosity molecular weight (Mv). The ratio of Mw to Mn characterizes the breadth of the molecular weight distribution, also known as "polydispersity." In order to fully characterize a polymer, both the average molecular weight, and the polydispersity must be defined.

Molecular weights of crosslinked polymers are also characterized by the backbone chain length (i.e. molecular weight) between adjacent crosslinks, Mc. Each network structure, (a single particle) may be viewed as a single molecule. The mass of the particle is the molecular weight, assuming all polymer chains are inter-connected by chemical bonds or crosslinks.

Measuring Molecular Weights

Molecular weights of *linear* polymers may be determined by appropriate physical measurements on very dilute solutions. Most commonly practiced methods are gel permeation chromatography (GPC) and intrinsic viscosity. Light scattering, ultracentrifugation, and osmometry are also used in the determination of molecular weight of polymers. However, all of these methods require the solubility of the polymer, and therefore cannot be used to determine the molecular weight of an insoluble, crosslinked polymer such as Carbopol®.

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In addition, routine spectrophotometric analyses such as ultraviolet (UV), infrared (IR), or nuclear magnetic resonance spectroscopy (NMR), can provide information about functional groups in a polymer. NMR has been used in protein analysis to develop three dimensional structural information. This method relies on good chemical shift separation between proton resonances. The primary sequence of amino acids is known through sequencing, and nuclear overhauser effect (NOE) experiments are used to develop spatial information. These experiments, plus molecular modeling have allowed 3 dimensional protein structures to be determined. Unfortunately, in the case of acrylic acid polymers, good chemical shift separation does not occur, and this method cannot be used on Carbopol®-type polymers.

Measuring the Molecular Weights of Crosslinked Polymers

The question of quantifying the molecular weights of Carbopol®-type polymers is quite complex, and there are no simple answers due to the random crosslinked network structure of the polymers. Unfortunately, whereas some naturally occurring polymers such as proteins have distinct primary, secondary, and tertiary structure, free radical polymers such as Carbopol®-type polymers are random polymers. This in itself makes the polymers difficult to study because structural information is necessarily an average of many different molecules. In addition the simple fact that these polymers are crosslinked makes direct structural studies difficult. To date we have not been able to determine either the molecular weight of the polymer chains or the distance between crosslinks.

Rheological Properties and Molecular Weights

While the relationships between structure and properties have been of interest both academically and in industry [1-6] few publications have attempted to characterize the structure-property relationships of Carbopol®-type polymers.[7-11]

Different grades of Carbopol® polymers exhibit different rheological properties, a reflection of the particle size, molecular weight between crosslinks (Mc), distributions of the Mc, and the fraction of the total units which occur as terminal units, i.e. free chain ends.

The molecular weights between adjacent crosslinks (Mc) are approximately inversely proportional to the crosslinker density. These may be calculated from the functionality of the crosslinking monomer, the relative ratio of acrylic acid to crosslinking monomer, and the efficiency of the crosslinking reaction, assuming negligible chain ends.[7] Alternatively, the molecular weight can be qualitatively compared to the rheological properties of a swollen gel and/or from the equilibrium swelling ratio. In simple terms, low viscosity, low rigidity polymer such as Carbopol® 910, Carbopol® 941, and Carbopol® 971P have a higher Mc, or conversely, have lower crosslinker densities. The higher the crosslinker level, the lower the equilibrium swelling ratio.

In the network theory of elasticity, the elastic modulus, G, is inversely proportional to the molecular weight between crosslinks (Mc). There have been attempts to extend the elasticity theory to swollen gels.[7,8,10] Based on this approach, Taylor calculated an Mc for Carbopol® 941 in the order of several million. This number is far too high as compared to the theoretical Mc calculated from the stoichiometry. Carnali and Naser estimated the Mc for Carbopol® 941 to be 3,300 monomer units (or 3,300 x 72 = 237,600 gm/mole) derived from a combination of dilute solution viscosity and equilibrium swelling. The Mc reported for Carbopol® 940 was 1,450 monomer units (or 1,450x72 = 104,400 gm/mole).[9]

What are the Molecular Weights of Carbopol® and Pemulen® Polymers?

When Carbopol® polymers have been polymerized under the same conditions, and using the same recipe as the crosslinked grades, but without the crosslinking monomer, the weight average molecular weights are in the order of about 500,000 as measured by gel permeation chromatography using linear polyacrylic acid as reference.

While the molecular weight of crosslinked Carbopol® polymer between adjacent crosslinks, Mc, is in the order of thousands, the actual molecular weight is in the billions. This is because each primary particle of crosslinked Carbopol® polymer can be considered as a single gigantic molecule, with the crosslinks attaching to many linear chains together. The molecular weight of such a molecule can be calculated from the size of

the primary particle and the density of the polymer. The calculated molecular weight for a crosslinked Carbopol® polymer with primary particle size of 0.2 micron could be as high as 4.5 billion due to the interlinkage of many polymer chains.

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