POLYMERIZATION

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Part 1. Principles of Polymer Chemistry

I. INTRODUCTION

Among the substances with which the chemist and the chemical engineer deal either in the laboratory or in industrial production is a group of materials which, although differing greatly in physical and mechanical behavior among themselves, show certain common characteristics and thus can be distinguished clearly from other chemical compounds. These substances, which can be characterized as rubbers, fibers, resins, or plastics, consist of molecules of high individual molecular weights which may vary from a few thousands up to the tens of millions. Thus, the over-all molecular weight of each of these materials can be expressed only as a statistical average of the total of the molecular species of which it consists. The molecules of each of these high-molecular-weight substances consist of a sequence of one or more basic units which are linked together in chains or networks of covalent bonds. The basic unit or units are called monomers, and the corresponding network or chain of linked monomers is known as a polymer.

While the primary emphasis in this chapter will be directed toward man-made polymers, it is important to remember that many natural products are polymeric. One of the most important of these is rubber, a form of polyisoprene with distinctive elastic properties from which its practical importance is derived. Other important natural polymers are silk, wool, gutta-percha, cellulose, starch, and all the natural proteins. It is a curious and interesting fact that natural polymers have not been obtained synthetically (with the possible exception of a recently prepared polyisoprene which has a structure similar to the natural one), even though the experimental conditions which can be employed in the laboratory may be varied and controlled to a much greater degree than the actual conditions under which these polymers are formed in nature.

One of the outstanding characteristics of low-molecular-weight materials is a sharp melting point. Polymers, however, have a more or less extended melting range[1] during which they pass through several stages, changing from a rigid solid to a rubber and then almost imperceptibly to a highly viscous liquid as the temperature is raised.

The reason that polymers do not possess a sharp melting point is twofold. First of all, the polymer is not made up of molecules of identical molecular weight, but contains a mixture of homologues of various degrees of polymerization.[2] Secondly, even if the polymer were of uniform molecular weight, the very size of its large molecules would prevent them from forming the perfect sharp melting crystals which are found in many low-molecular-weight materials.

Of the various types of physical measurements which can be employed to characterize nonpolymeric molecules, certain ones are of primary importance. Among these are freezing-point depressions, vapor pressures, boiling points, and crystal structure. These measurements are suitable only to a limited extent for the characterization of polymeric materials, and other physical methods have to be employed to obtain satisfactory results. Of particular usefulness are studies of polymer solutions, which yield data on their viscosity, osmotic pressure, light scattering, and sedimentation in the ultracentrifuge. The experimental results gathered from these investigations provide much useful information about the polymers themselves.

The reason that methods conventional for low-molecular-weight compounds prove unsatisfactory for polymers arises from the fact that the polymer molecule is so much larger than the monomer. Such measurements as freezing-point depressions, for example, which are easy to carry out for molecules of a molecular weight of 500 or less, and which give satisfactory results, show only an insufficient magnitude of the effect for high polymers and do not allow exact determinations. Contrariwise, ultracentrifugation, for example, is applicable only for materials where the individual molecules are sufficiently large, and diffusion is not accentuated by too active Brownian motion.

X-ray and electron-diffraction analysis of high-polymeric materials show that the molecules in some of them are arranged in a state of complete disorder (amorphous state); others exhibit a high degree of order (crystalline and oriented states). In most cases the diffraction diagrams indicate the simultaneous existence of ordered and disordered domains. Intensive studies relating the properties of high polymers to the spatial arrangement of their molecules show this to be one of the major factors which determine their physical and chemical behavior.

Other contributing factors are the average molecular weight, the molecular-weight distribution function, the chemical composition of the polymer, and the spatial arrangement of substituents along the molecular chain.

Among the most important of the properties of polymers from a practical and industrial point of view are their high-temperature and low-temperature behaviors. Some of them soften upon heating and regain their original hardness upon subsequent cooling, whereby the heating and cooling cycle can be repeated at will. These materials are called *thermoplastics*. Others become insoluble and infusable after the first heating and decompose on further increase in temperature. These are called *thermosetting materials*. Many polymers tend to become brittle and unworkable at low temperatures; on the other hand, softening ranges of other polymers are often too low and inadequate for specific industrial application. Therefore the improvement of softening temperatures for thermoplastics, the resistance of thermosettings to high temperatures without charring and decomposition, and, finally, the avoidance of brittleness and stiffness of rubbery and flexible polymeric materials at low temperatures have been the subject of most intensive research by industrial polymer chemists.

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