

COPOLYMERS

Polymers (“poly”=many; “mer”=unit) are long-chain molecules that consist of “many units”, i.e., repeating sections of monomers --- like links in a chain --- e.g., polyethylene would consist of many ethylene $(-\text{CH}_2-\text{CH}_2-)$ units. These monomers can be added one to another to create longer and longer molecules --- a term which we refer to as molecular weight.

If two or more compatible monomers (e.g., ethylene and propylene) can be polymerized and added to the same polymer chain, the two monomers are considered to be comonomers and the resultant polymer is called a copolymer. Now, that’s the simple idealistic approach to copolymers.

In actuality, there are a lot of ways comonomers can add together. The ideal approach, which very seldom happens, is an alternating copolymer chain. Comonomers may also add in a “random” or “statistical” arrangement. This too tends to be a somewhat idealistic model unless synthesis is highly controlled. While a random addition seems relatively easy to achieve, there are generally differences in the reaction rates of the two monomers. Therefore, polymer segments which initiate first tend to be high in composition of one monomer (the monomer which polymerizes faster or more easily), while those segments that are formed toward the end of the polymerization tend to consist of more of the other monomer. Therefore, uncontrolled “random” copolymerization will usually yield a copolymer which consists more of “blocks” of one monomer or the other --- these are referred to as block copolymers.

Intentional polymerization of block copolymers, usually consists of polymerization of one monomer, then introducing a second monomer, and sequentially adding another block to the chain. The simplest block copolymer is the “diblock” where one end of the chain is one type of polymer, while the other end is another type. Triblocks would add yet another block of polymer to the chain to form an A-B-A or B-A-B structure. Comonomer blocks can also be added as branches to the main chain, or as arms in a star-like pattern off of a central segment. In this way an infinite arrangement of polymer structures can be obtained --- each with some unique properties. These types of structures are used in many of the TPEs (thermoplastic elastomers).

In ABS, styrene and acrylonitrile are copolymerized in the presence of polybutadiene rubber particles. The styrene and acrylonitrile copolymerize into a random copolymer of SAN, some of which “graft” or grow as branches on the surface of the polybutadiene rubber particles. These branches are the only true “terpolymer” molecules in ABS, and they act as compatibilizers between the polybutadiene rubber particles and the SAN matrix. So while ABS is often referred to as a terpolymer (which it technically is), its mechanical behavior is derived from the fact that its composition is more like that of a polymer blend, a blend of discrete polybutadiene rubber

particles in a matrix of SAN (styrene-acrylonitrile) copolymer. The minor amount of terpolymer grafts act only as the “glue” to hold the system together.

Books have been written on copolymers, so there's a lot more that could be said, but the key point here is when trying to understand the behavior of polymers and copolymers, the idealistic model is probably an incorrect assumption. Copolymers are not generally alternating sequences of comonomers; random copolymers generally consist of many small uncontrolled blocks of the two monomers, and may be tapered --- having the initiating section higher in content of one monomer, while the terminating end is richer in the other monomer. In impact copolymers, such as HIPS and ABS, the only co- or terpolymer that exists is present at the rubber-matrix interface; the bulk of the system is a blend of two polymer systems created insitu (during the polymerization).

Rich Geoffroy
POLYMER SERVICES GROUP