PROBLEMS IN THE SYNTHESIS OF BLOCK POLYMERS BY ANIONIC MECHANISM

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The recently developed "thermoplastic elastomers" owe their properties to their block polymer structure. As is well known, these can be defined as SDS block polymers, where S represents a polystyrene block while D represents a polydiene block (generally butadiene or isoprene). The result is that these linear polymers show similar behavior to that of crosslinked networks, presumably due to the fact that the polystyrene end blocks aggregate into "domains", because of their incompatibility with the polydiene, and these glassy domains can act as "network" junctions at ambient temperatures.

Recent studies have shown that this is indeed the morphology which is found in these systems. Furthermore, the physical mechanisms which operate in these systems and the effect of the molecular architecture on these mechanisms has now been considerably elucidated. It appears that, in order to attain the optimum elastomer properties, the block lengths are fairly well prescribed, the polystyrene being in the range of 10,000-15,000 in molecular weight, while the polydiene should be in the 50,000-100,000 range. Furthermore, the elastic properties and tensile strength of these materials appears to depend on the ability of the polystyrene domains to absorb the applied stresses, undergoing an inelastic deformation in the process. Hence it is obvious that these properties will depend greatly on this domain formation, which is, of course, a function of the incompatibility of the two types of blocks. The latter, in turn, depends not only
on the chemical nature of the blocks but on their size, especially in the ranges indicated, e.g., polystyrene blocks below 10,000 in molecular weight may result in a drastic decrease in tensile strength of the material. It is therefore important to realize that such factors as block size distribution and efficiency of block polymer formation can have a profound effect on the final properties of these materials. The polymerization system used for the synthesis of these polymers must therefore meet certain specifications.

The synthesis of block polymers, such as SDS, having a precise and predictable structure, only became possible with the advent of homogeneous anionic polymerization of the non-terminating type. Such "living" polymers have made it possible to use four different approaches to the synthesis of SDS polymers, based on type of initiator used:

1. Difunctional initiators, e.g., sodium naphthalene, leading to a "two-stage" process (i.e., polymerization of D followed by polymerization of S).
2. Three-stage process, using monofunctional initiators, e.g., alkyllithium.
3. Two-stage process, using monofunctional initiators to synthesize SD diblocks and subsequent coupling to SDS.
4. Two-stage process, with alkyllithium initiators, involving formation of an initial S block followed by copolymerization of the styrene and diene, in which the latter is preferentially polymerized.

Each of the above methods has advantages and disadvantages which have a direct bearing on the quality of the final polymer. These will be considered, with special reference to the SDS polymers, in connection with the following parameters: a) initiation and termination problems, b) microstructure of polydiene.

1. Difunctional Initiators
   These initiators, e.g., sodium naphthalene, dilithium compounds, etc., are, in principle, best for the synthesis of ABA block polymers, on two counts. In the first place, they involve only a two-stage process, i.e., the sequential addition of two monomers, B followed by A, thus minimizing any termination of blocks by adventitious impurities present in the monomers. It should be noted that termination of a B block at one end only will lead