

SYNTHESIS OF BLOCK, GRAFT, SEGMENTED AND ION-CONTAINING COPOLYMERS

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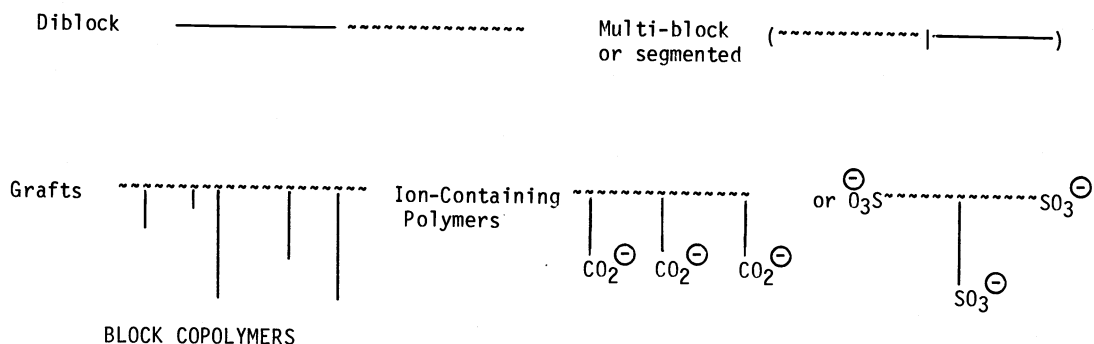
Abstract - Multiphase polymeric materials may be prepared as block, graft, segmented or ion-containing copolymers. This review provides a discussion of the important synthetic techniques that may be utilized to prepare these materials. The review includes critical comments on synthetic processes reported in the literature. Block copolymers have been prepared principally by living anionic mechanisms into various architectures, including di-, tri- and star-shaped structures. Multiple blocks, or as they are more commonly known, segmented systems, have produced important materials via polyurethane, polyester-ether, and siloxane chemistry. The general features and architectural microstructures possible are reviewed. Graft copolymers have been utilized traditionally to prepare rubber toughened thermoplastics such as impact polystyrene and ABS. Such materials though valuable, tend to be relatively ill-defined due to the free radical nature of the grafting reactions. More recently, the approach of preparing so-called macromonomers has been introduced by Milkovich and coworkers. Here, one attempts to provide a polymerizable unit at the terminal of a chain. Incorporation of two or more ordered grafts in a subsequent free radical copolymerization has greatly expanded the utility and definition of graft copolymerization. Indeed, many reports have appeared around the world that have utilized this technique in the last two or three years. Lastly, techniques to produce ion-containing copolymers are reviewed. These systems are usually prepared either by direct copolymerization in the case of carboxyl containing systems or via post-reactions for sulfonated ion-containing systems. Quite recently, attempts have been made to provide much better defined location of the ion-containing groups through cationic, step-growth (the "halato" materials) and by well-defined anionic polymerization followed by subsequent hydrolysis of bulky alkyl methacrylate groups. Such ion-containing polymers show promise in allowing for the first time a model system that is suitable for detailed characterization studies. In summary, the multi-phase syntheses described in this review encompass a variety of important materials which can only be expected to expand significantly in the future.

INTRODUCTION

Multiphase polymer systems have received widespread attention in recent years. These materials may be synthesized in the form of block, graft, segmented, or ion-containing copolymers or as blends; all of these materials are usually characterized by the presence of two or more polymeric phases in the solid state [1-17].

Polymer blends or alloys effectively competed with new polymers and copolymers as cost effective materials during the last decade [2,3]. However, the majority of homopolymer pairs are immiscible with one another and give rise to low strength materials due to the lack of interfacial adhesion between the separate phases. Block, segmented, graft and ion-containing copolymers offer several advantages over blends even though they are no doubt more expensive than simple blends. Since the multiphase materials are covalently bonded together, macroscopic incompatibility at the interface is minimized. Secondly, molecular architecture can be designed to produce novel materials. Thirdly, the subject copolymers can be used to strengthen blends of immiscible polymers by serving as "emulsifiers" [1,2,3], which improves the interfacial adhesion and mechanical properties. This paper will review aspects of block and segmented copolymers, some important areas of ion-containing polymers and grafting. In particular, grafting via the recent "macromolecular monomer" routes will be discussed. The structures of interest here are outlined in Scheme 1.

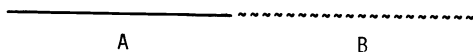
SCHEME 1. Schematic representation of blocks, graft, segmented and ion-containing polymers.



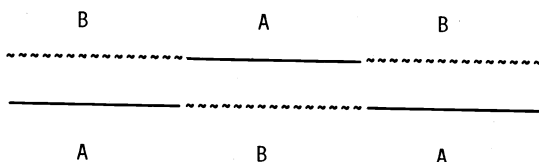
Block copolymers represent an important area of polymer science which has been conceptually known for about some time [1]. However, the field was not well appreciated until elastic linear polyurethanes were developed which were composed of "soft" polyester segments and "hard" polyurethane sequences but were nevertheless soluble in organic solvents. Somewhat analogous polyester-type polymers with similar properties were also prepared at about the same time. The development of well-controlled living anionic polymerization [18-23] techniques further permitted the synthesis of architecturally well-defined block polymers.

Living anionic polymerization was also used successfully to prepare di- and multiblock structures. However, the important difference between a triblock [1] and diblock structure [2] in determining polymer properties was not recognized until the discovery by Milkovich and Holden [17,24-26], which showed the importance of obtaining a triblock architecture. This was followed by a series of extensive investigations, which have been reviewed [1,4,14,15].

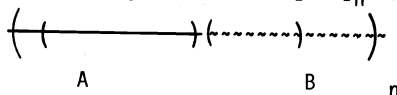
Four basic types of linear block copolymer structures can be identified. Using A's and B's to denote dissimilar chemical structures, one may define an A-B diblock copolymer as:



The addition of a third block produces an A-B-A or B-A-B triblock copolymer.

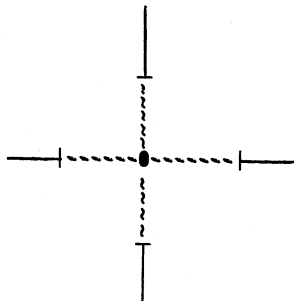


Coupling four or more blocks together gives rise to $[A-B]_n$ multiblock or



$n = 2, 3, 4, \dots$

segmented copolymers where n is greater than 1. In addition, diblock copolymers may be coupled at a single junction point to form radial or star block copolymers [27-29] as illustrated below for a "four-arm" system.



The unique elastomeric behavior of A-B-A and $-(A-B)_n$ block copolymers was responsible for the development of the new technology termed thermoplastic elastomers. Block copolymers of this type are characterized by a combination of features that were previously considered to be mutually exclusive, namely, thermoplasticity coupled with rubberlike behavior. Several commercial products of this type are available including the Kratons, Hytrel and Estane materials. The key requirements for achieving thermoplastic elastomeric behavior is the ability to develop a two-phase physical network. Such a system is composed of a minor fraction of a hard block (i.e., T_g or T_m above room temperature) and a major fraction of a soft block (i.e. T_g below room temperature). In these systems, the hard blocks associate to form small morphological domains that serve as physical cross-linking and reinforcement sites. The tri-blocks ordinarily are physically crosslinked via glassy domains, but semi-crystalline materials are also known [16]. These sites are thermally reversible, i.e., melt processibility is possible at temperatures above the hard block T_g or T_m . Only architectural forms that contain two or more hard blocks per macromolecule are capable of producing this effect. Therefore, all block copolymer thermoplastic elastomers are based on A-B-A or $-(A-B)_n$ or $(AB)_x$ star sequential arrangements. Diblock copolymers are incapable of producing network structures, since only one end of the soft block is chemically linked to a domain of hard segments.

Many approaches for synthesizing polymers with "blocklike" character have been reported. However, only a few actually are capable of producing legitimate block copolymer structures. Others do not result in predictable or well-controlled architecture. All of the successful techniques are forms of either living anionic chain reaction polymerization or step-growth (condensation) polymerization. The success of these techniques stems primarily from three desirable features, common to both approaches. First, the location and concentration of active sites are known. Second, homopolymer contamination is minimal. This results from the absence of terminating side reactions in living systems and from stoichiometry control in the step-growth systems. Finally, segment length and placement are controlled. This is accomplished by sequential monomer addition techniques in the living polymerizations and by the judicious selection of oligomer end groups and oligomer molecular weight in the step-growth case.

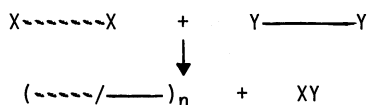
Living polymerization processes may entail only initiation and propagation steps and can be essentially devoid of terminating side reactions. This feature allows the synthesis of predetermined and well-controlled structures, which is a valuable asset in the preparation of block copolymers. Structural control is often critical in order to develop the unique properties inherent in block copolymers. There is a wide spectrum of systems that can, in theory, be synthesized by this method. Some of these systems approach the above ideal situation quite closely. Others deviate from this ideal to varying degrees. Ring opening polymerizations can be carried out via living processes [18,28-30] and can proceed, at least in principle, via anionic, cationic, and coordination mechanisms [29,32]. The anionic route is inherently more free of terminating reactions due to the greater stability of the growing ends. Therefore, this technique is often preferred for synthesizing block copolymers.

SEGMENTED OR MULTI-BLOCK COPOLYMERS

The interaction of functionally terminated oligomers is a versatile method for producing segmented copolymers. Many functional groups can be utilized, at least in theory. By this approach, only the intersegment linkage is formed during the block copolymerization reaction. Generally, difunctional species are used leading to $-(A-B)_n$ multi-block copolymer structures only. The preformed oligomers can be prepared either by step-growth reactions or by appropriate chain reaction or ring opening polymerizations. In the step-growth case, the end groups are a natural consequence of the polymerization chemistry and hence bear the end group of the monomer used in excess.

In the case of ring opening or chain reaction polymerization, the end group can be predetermined via initiator choice or by end capping. Possible systems include polyamides, polycarbonates, polyurethanes, polysiloxanes, poly(alkylene ethers) and poly(aryl esters). Useful end groups include amines, isocyanates, acid halides, silyl halides, hydroxyl, silane and even carbanions. The major requirement is that they interact in a highly efficient manner.

The above described functionally terminated oligomers can be incorporated into $-(A-B)_n$ block copolymers with perfectly alternating segments or with statistically placed segments. The differences here do not seem to be widely appreciated (1). Perfectly alternating sequence distributions are obtained when oligomers bearing mutually reactive end groups are used. By definition, such oligomers can only react with each other and not with themselves. This technique is typified by the general synthesis shown below.



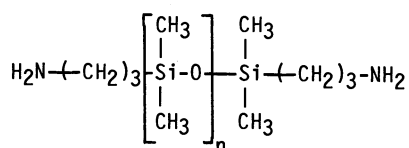
The average molecular weights of the above blocks are identical to those of the corresponding oligomers. Although these segments occur in a perfectly alternating sequence, the polydispersity of the block copolymer is, of course, a function of both the oligomer-forming and block copolymer-forming reactions. In contrast, block copolymers with less control of segment sequence are obtained when two oligomers with the same functional end group are coupled via reaction with a third component. If both oligomers are similar in reactivity toward the coupling agent, they are incorporated into the block copolymer molecule in a statistical or random fashion. A typical example of this is the coupling of hydroxyl-terminated oligomers by phosgene or diisocyanates. A result of the above reaction scheme is that the average block molecular weights must be higher than those of the corresponding oligomers. This is due to the ability of a given oligomer to couple with itself as well as with the second oligomer. If the two oligomers are greatly different in their reactivity toward the coupling agent, it is possible to produce structures that contain long runs of similar segments. The chemical composition of the perfectly alternating systems is directly proportional to the oligomer molecular weights. By contrast, the statistically coupled systems have the advantage that compositions can be easily controlled since they are independent of block molecular weight. In the alternating systems, equimolar quantities of the functional oligomers are required in order to fulfill stoichiometric requirements. In the statistically coupled systems, any combination of the two oligomers can be stoichiometrically satisfied by the use of the appropriate quantity of coupling agent.

A third method involves polymer growth from the oligomer end groups. This technique is essentially a combination of the two techniques described above in that the copolymer forming reaction employs both monomers and preformed functionally terminated oligomers. Polyurethanes and urea-linked systems are usually prepared in this manner [1,4,14,15]. In general, this route may be more economical than the oligomer-oligomer approach, since it allows the possibility of bulk polymerization and does not require the isolation of the second oligomer. Bulk polymerization is not normally possible with the oligomer-oligomer process due to the well-known phenomenon of polymer-polymer incompatibility [1-3]. Furthermore, this technique has an advantage in the solution polymerization of copolymers containing both amorphous and crystalline segments. This combination may be difficult to achieve by the oligomer-oligomer process due to the insolubility of the crystalline segment. However, one may accomplish this by growth of the crystallizing polymer initiated by the end groups of a preformed soluble oligomer.

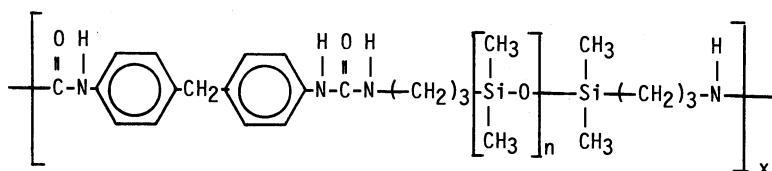
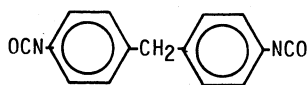
Block or segmented copolymers can be prepared by this technique from various combinations of starting materials. For example, polycarbonate-polysulfone or aryl ester-aryl ethers [31-33] and a variety of siloxane copolymers [34-40] have been produced in our laboratory.

The linkage between the blocks is formed simultaneously with the growth of the second block. The nature of this linkage depends upon the end group of the preformed oligomer, which in turn is a function of the initiator, capping agent, or comonomer stoichiometry employed.

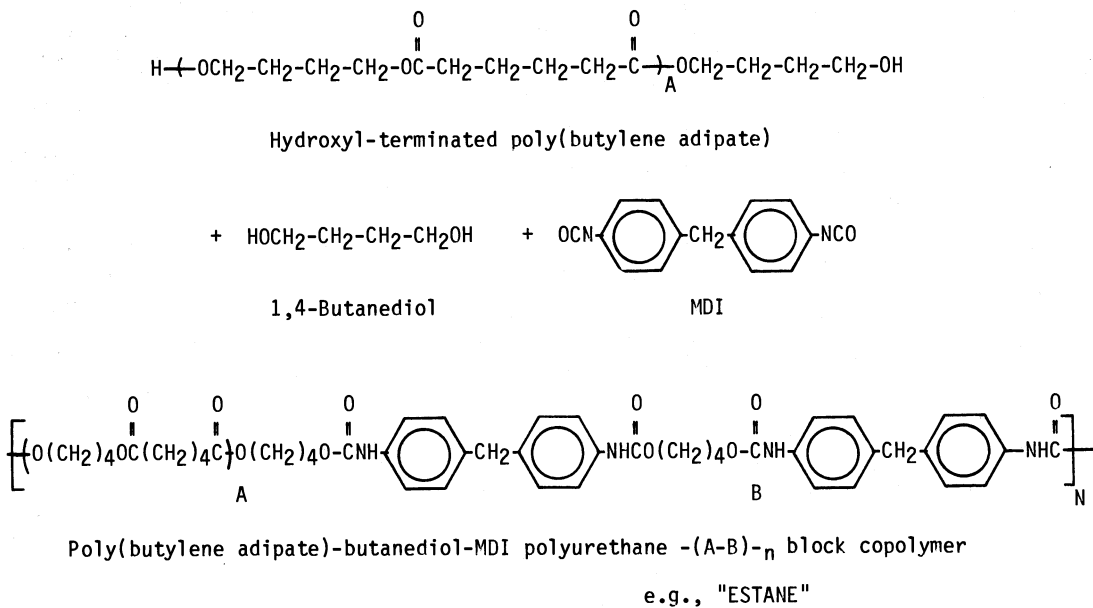
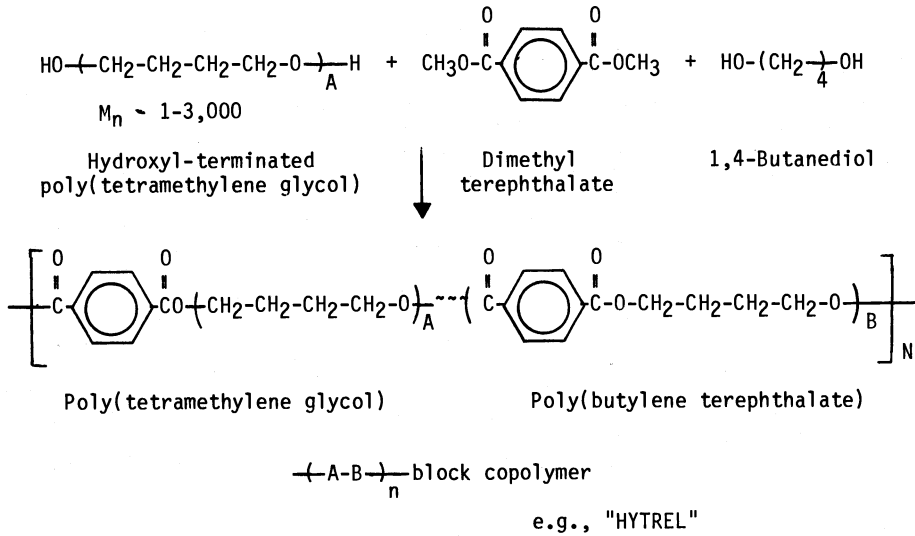
Recently [38-40] a series of unusual segmented siloxane copolymers were reported, where apparently strong hydrogen bonds in the urea link are capable of providing strength and mechanical stability to well above 100°C. The synthesis of one such system is outlined below.



$n = 1$, DSX
 $n > 10$, PSX



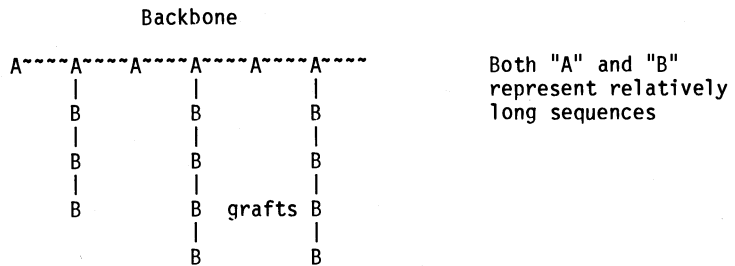
The oligomer-monomer(s) approach can be used to prepare many segmented copolymers. Two commercial examples are shown below. The structures are idealized, since sequence distribution effects would be significant.



GRAFT COPOLYMERS

Traditional Approaches

All graft copolymers are comprised of two general structural features: a backbone of polymer "A" to which a number of "B" sequences are grafted, such as shown below.



There is considerable latitude as to the chemical nature of the backbone and the grafted segments and the techniques for joining them. This class of polymer hybrid provides the basis for a number of commercially important polymeric materials, such as impact polystyrene, ABS (Acrylonitrile-Butadiene-Styrene), and methacrylate-butadiene-styrene (MBS).

Graft copolymer technology has been discussed in a number of books and reviews [41]. It is our intent not to treat this subject in detail here, but rather to present some highlights of the current state-of-the-art.

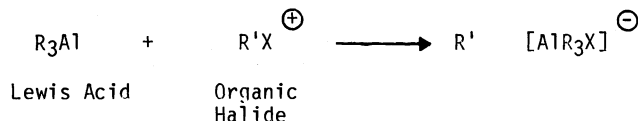
Graft copolymers are generally prepared by the free radical, anionic, or cationic addition (or ring opening) polymerization of a monomer in the presence of a preformed reactive polymer. Free radical techniques have received the greatest amount of attention in the literature and are the most commonly used commercially. Free radical techniques are industrially most important and can be subdivided into two general categories. The first involves the polymerization of an olefinic monomer in the presence of a preformed polymer bearing labile hydrogen, e.g., grafting of styrene onto polybutadiene. Initiation is achieved with peroxides, irradiation, or thermal methods. Abstraction of the labile hydrogen by the peroxide initiator or the growing chain during the polymerization produces radicals on the backbone. The link between the graft and the backbone can be formed via monomer initiation by the backbone radical or by recombination reactions. The second category features initiation of the monomer by hydroperoxide or functional groups already on the preformed backbone.

Free radical polymerization is the oldest and most widely used technique for the preparation of grafted materials [1,17,41]. However, free radical techniques generally lead to rather ill-defined products. Therefore, we will limit this discussion to just a few developments.

As is well known, nearly all large volume impact modified styrene materials involve, at some point, a grafting of the vinyl or alkenyl aromatic monomer onto a polydiene rubber. Therefore, improved understanding of this process is certainly one of the most important tasks facing the polymer chemist. Recently, some very thorough studies in this direction have been undertaken and, as a result, some additional insight has been gained [41].

Better control of structure and less homopolymer contamination may be possible by ionic rather than radical grafting mechanisms. The aluminum alkyl-initiated cationic grafting of isobutylene onto the allylic and/or tertiary chloride sites present in poly(vinyl chloride) is one example of this technique [42,43].

One of the major methods for generating organic cations consists in forming a complex between a Lewis acid and an organic halide containing, preferably, a labile carbon-halide bond.



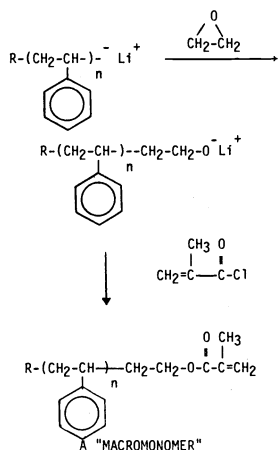
This was utilized successfully for the preparation of PVC backbone-graft copolymers. PVC contains labile allylic chloride sites and is, therefore, amenable to the scheme shown above. The cation formed via that route serves as the polymerization macroinitiator [42,43].

Anionic grafting techniques are known [18-23] and can also be subdivided into two general categories involving grafting via (a) backbone initiation and (b) backbone coupling. Anionic techniques have also been applied to the synthesis of backbones, side chains, and the graft copolymers themselves.

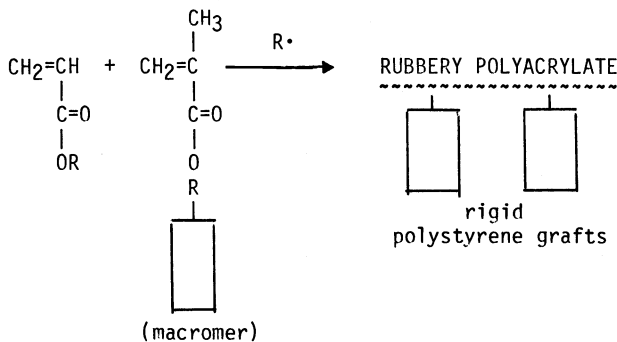
Graft copolymerization of pivalolactone initiated by pendant carboxylate groups has been demonstrated to produce interesting materials [29,51,52].

Graft Copolymerization Involving Macromonomers

Milkovich and coworkers discovered [24,44,45] that novel and interesting graft copolymers can be prepared that have potential as thermoplastic elastomers or rigid tough elastoplastics. One example of this method is outlined below.



The macromonomer here would be perhaps 10-20,000 $\langle M_n \rangle$, and hence behave as a glassy, rigid, nearly monodisperse chain capped with an active, polymerizable unit. This may be contrasted with the very polydisperse grafts in impact polystyrene [41]. It has been demonstrated [24] that subsequent "copolymerization" with conventional monomers may proceed to produce rubbery, polystyrene toughened multiphase materials. The method thus greatly expands the list of potential systems. An example of a graft copolymer prepared from the macromonomer is shown below.



The macromonomer concept has excited many scientists around the world. Already many papers have been published utilizing cationic [42,43] free radical transfer [46] and anionic [47] methods.

Many additional studies are also now appearing in the literature, which utilize various capping agents and polymerization mechanisms.

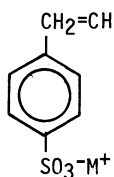
Ion Containing Copolymers

Ionomers, which contain 10 mole % or less amount of ionic groups on a non-polar backbone are one of the most interesting classes of polymeric materials [48-50]. The presence of small amounts of these ionic groups exerts a profound effect on the properties of the resultant materials due to associations. Although there is a variety of ionic functionalities that can be incorporated into polymers, groups such as carboxylates, sulfonates and to a lesser extent, phosphonates and quaternary ammonium salts are the most important.

There are basically two methods for the preparation of ionomers. One is the "Grafting" of an ionic substituent onto a preformed polymer and the second one is the "Direct Copolymerization" of a hydrocarbon monomer with an unsaturated organo-acid or salt. Most of the carboxylated ionomers are prepared by the direct copolymerization of acrylic or methacrylic acids with the vinyl monomers [53]. The copolymers produced are then either partially or completely neutralized with bases in order to incorporate different counterions (e.g. Na^+ , K^+ , Zn^{++} , etc.) into the system. On the other hand, post-polymerization reactions are generally employed for the introduction of sulfonate groups into the structure of an ionomer [54-59]. This method is more difficult and time consuming than the former. Therefore, although sulfonated ionomers are known to exhibit superior properties relative to the corresponding carboxylated copolymers [58], synthesis of these ionomers on industrial scale has not been achieved. There is also relatively little work in the literature on the direct copolymerization of sulfonated monomers with conventional vinyl monomers.

One major difficulty in the direct copolymerization of sulfonated and vinyl monomers is the great difference in the solubilities of the ionic and covalent monomers. This makes it almost impossible to find a common organic reaction solvent. Moreover, chain transfer to the solvent is also a problem. Therefore, conventional methods of homogeneous polymerization can not easily be applied.

In our laboratories we are investigating the direct copolymerization of sulfonated styrene with various alkyl acrylates, dienes, styrene and fluorinated vinyl monomers. We also



employ emulsion polymerization and have preferred to utilize a water soluble initiator system. Some of our results on the direct copolymerization of sodium styrene sulfonate and n-butyl acrylate systems were recently reported [60]. The results clearly showed that one is able to convert weak acrylic ester polymers to very strong elastomers (ionomers) in high yields by our method.

In essentially all of the ion-containing polymers studied to date, the unanswered questions related to microstructure have frustrated detailed characterization and model development studies. Recently, relatively well defined terminal [42,61] or segmented [62,63] ion containing polymers have been produced which have interesting properties. In addition, we have recently prepared di-block [64] and triblock copolymers wherein controlled molecular weights, compositions and narrow molecular weight distributions can be defined via anionic polymerization. The block system thus prepared may be partially or completely hydrolyzed. In essence, the bulky alkyl methacrylate block is converted to a methacrylic acid block. Ionization of the carboxyl groups allows the conversion to ionic groups whose position and concentration can be predetermined. We are hopeful that these systems will serve as model structures which will further permit elucidation of the morphology of these interesting systems.

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