ACRYLONITRILE BLOCK AND GRAFT COPOLYMERS

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Abstract—This paper presents a review of the methods available for preparing block and graft copolymers in which one component is acrylonitrile. Methods using polymer ions and polymer radicals are considered together with a useful new technique based on reactions of nitrile groups with amide compounds of group IV transition metals.

Because of its polarity and its unusual solubility properties, a polyacrylonitrile component adds great potential interest to a block or graft copolymer system and many reports can be found in the literature of attempts to prepare such copolymers. The methods used embrace a wide range of techniques; some are purely chemical,1-3 others involve ultrasonics4 or high energy radiation.5 My main purpose in this paper is to discuss three of the purely chemical methods which have developed significantly in recent years, and the methods in question involve polymer ions, polymer radicals or organometallic polymer derivatives as key reagents in the formation of the block or graft copolymer.

METHODS USING POLYMER IONS

The living polymer systems described by Szwarc6 provide the best-known technique for preparing block copolymers but not much is recorded in the literature concerning molecules containing acrylonitrile as one component. The use of acrylonitrile as the first-phase monomer with either lithium butyl or sodium naphthalene amide, is added to the second-phase monomer; the latter a small proportion of swelling agent, such as dimethylformamide, is added to the second-phase monomer; the latter.

Block copolymers of styrene and acrylonitrile were prepared by Perry7 using a different technique. He made polystyrene in a free radical system with molecular growth controlled by transfer to dibutylphosphine so that he obtained an initial P of about 400 with 95% of the polystyrene chains containing a phosphine residue at one end. Since dialkyl phosphines initiate the anionic polymerization of acrylonitrile, the first-phase polymer is ideally suited to form the basis of block copolymer and acrylonitrile contents in the range 14-76% were obtained. Extraction techniques established a fairly high purity level for the block copolymers thus obtained.

METHODS USING POLYMER RADICALS

During the investigation of the bulk polymerization of acrylonitrile it was deduced from kinetic observations that under certain conditions a significant, or even substantial, fraction of the radicals generated remain occluded in the precipitated polymer for long periods of time.6,11 At temperatures as high as 60°C occlusion affects the velocity constant for the termination process but is not severe enough to trap radicals; at 25°C, on the other hand, it has been estimated that perhaps 1% of the radicals generated in photopolymerization become so tightly embedded in the polymer that they are unable to propagate further, although they are liberated by raising the temperature.

Very fine control is possible in this situation because elevation of the temperature to 40°C facilitates propagation but does not sufficiently open the structure that the occluded radicals terminate in appreciable numbers, whereas heating to 60°C destroys them all in a short time. The environment of the trapped radicals can be changed by replacement of the residual acrylonitrile by another liquid, and if this contains a monomer the liberated radicals will react with it to produce block copolymer.12 The precise nature of the block copolymer will then depend upon the mechanism which terminates the new growth, disproportionation or transfer giving an AB type and combination an ABA type of block structure.

The type of system discussed here was first described by Bamford and Jenkins,12 who demonstrated that the nature of the second monomer had a large influence on the extent of second-phase polymer formed. This is, of course, not surprising since the system must be very sensitive to the degree of interaction between the liquid and the polymer, a point taken up later by Seymour and his colleagues.13 Among the systems examined by Bamford and Jenkins,12 the one which gave the greatest amount of polymer was polyacrylonitrile/methyl acrylate; it was possible here to attain almost complete conversion of the methyl acrylate to polymer because the rate of radical destruction is very low.

This observation highlights a key factor in the situation, viz. that if polymer and liquid interact too weakly the occluded radicals will not be liberated enough to propagate, while swelling on too large a scale will allow the radicals to terminate too rapidly to produce much block copolymer. In the former case a remedy is at hand if a small proportion of swelling agent, such as dimethylformamide, is added to the second-phase monomer; the latter problem can possibly be mitigated by mixing the monomer with a liquid which has very little interaction with polymer or by lowering the temperature, but these
factors also tend to limit the extent of polymerization.

The original work was followed up by Hiemeeleers and Smets who showed that the molar uptake of second monomer by polyacrylonitrile radicals was below 5% with styrene, vinyl acetate, acrylamide and vinylidene chloride, a little higher with methyl methacrylate (9%) and more substantial with methyl acrylate in dioxane (14%) and acrylic acid (16%) but that none of these monomers challenged acrylonitrile itself (36%). Thus bulk methyl acrylate seems to be an exceptionally favourable case. These authors made the helpful observation that only very small quantities of second step homopolymer are formed in the process, but of course a drawback to this method of preparing block copolymers is the homopolyacrylonitrile, from association with which the block copolymer requires to be extracted.

Other heterogeneous polymerizations than that of acrylonitrile were tried as the basis of this method of block copolymer formation, the photopolymerization being carried out at 25°C. With polyacrylamide only small amounts of second monomer were observed to become attached and with polyvinylchloride none. This confirms the general belief that trapped radicals are not obtained in these systems above the glass transition temperature (presumably the Tg measured in the particular system rather than that of the dry polymer). Seymore has placed considerable emphasis on the importance of the relationship between solubility parameters of the first-phase polymer and the second-phase medium. While it is true that such a correlation does exist, so that a difference of less than 3-1 Hildebrand units is necessary for penetration of polymer by liquid to recur, the original observations on acrylonitrile polymerization indicate that temperature could also be a crucial factor but there does not seem to be a sufficient body of systematic data at the present time to test this possibility.

More recently Seymore et al have reported that the addition of fumed silica to the first-phase polymer facilitates the preparation of block copolymers.

METHODS USING ORGANOMETALLIC POLYMER DERIVATIVES

In recent years we have studied a new system for the polymerization of acrylonitrile which affords a useful method of preparing both block and graft copolymers with acrylonitrile as the second phase. A brief description of this system will be presented as a basis for discussing the preparation of the binary molecules.

Compounds containing bonds between group IV transition metals and nitrogen act as very efficient and specific initiators for the polymerization of monomers containing CN groups, that is, for acrylonitrile and methacrylonitrile. The former monomer is much more active than the latter but both respond to the initiators which themselves increase markedly in activity from Ti-N to Zr-N. Most of our work has been carried out with Ti-(NMe2)3 and this compound, designated T3, will figure in the summary below.

Polymerization of acrylonitrile takes place smoothly when the monomer is mixed with T3 in a simple hydrocarbon solvent at room temperature. It is necessary to dry all reagents thoroughly and to exclude oxygen but a nitrogen blanket is adequate for the latter purpose. The solvent is preferably methyl cyclohexane because the low freezing point of this substance affords a large liquid range over which to study the influence of temperature. Using concentrations of T3 = 10-3 M and [AN] = 1 M polymerization reaches 50% conversion in less than 50 min at 25°C.

Extensive studies of the reaction mechanism have led to the conclusion that the reaction follows the following sequence:

\[ \text{Ti} - \text{N} + \text{CH}_3 + \text{CH} = \text{CH} \rightarrow \text{Ti} - \text{N} \equiv \text{C} - \text{N} + \text{CH}_3 \]

\[ \text{CH} = \text{CH}_2 \]

\[ \text{Ti} - \text{N} \equiv \text{C} - \text{N} + \text{CH}_3 + \text{CH} = \text{CH} \rightarrow \text{Ti} - \text{CH} = \text{CH} - \text{N} \equiv \text{C} - \text{N} + \text{CH}_3 \]

\[ \text{CH} = \text{CH}_2 \]
Propionitrile will give the compound the various steps. The evidence for this mechanism has been discussed in some detail elsewhere and it seems that the equations above represent the essential steps in the process. Of course, since the initiator Ti contains four Ti—N bonds there may be multiple activity at the transition metal centre, indeed it is clear that such is the case.

Some very useful information has been derived from the use of propionitrile as a model substance which should be able to undergo only step (1) of the sequence shown but in the present context it does not matter whether the monomer reacts in the 1,4 mode or at the —CN group alone.

The first step in the reaction between Ti and propionitrile will give the compound

\[
\begin{align*}
\text{Ti} - \text{CH—CH—N=CN} + \text{CH}_{2} = \text{CH} \rightarrow \text{Ti} - \text{CH—CH—N=CN} + \text{CH}_{2} = \text{CH} \\
\text{CN} & \quad \text{CN} \\
\text{CH=CH}_{2} & \quad \text{CH=CH}_{2}
\end{align*}
\]

which is the propionitrile analogue of compound Ti in the reaction scheme. It would seem entirely possible that this compound should also be able to promote step (2) by reaction with acrylonitrile monomer, and such is indeed the case. If Ti and propionitrile are mixed together and allowed to react for a few hours the mixture proves to be a second-phase monomer. At this stage the mixture left to react so that acrylonitrile grafts could grow on the polystyrene backbone. In this way it proved possible to add grafts of polyacrylonitrile equal in total weight to that of the polystyrene backbone. Since the molecular weights of styrene and acrylonitrile differ by almost exactly a factor of two this means that the final polymer was roughly 2:1 acrylonitrile: styrene on a molar basis.

(ii) Block copolymer

Polystyrene was prepared using azo-bis-isobutyronitrile as initiator under conditions where very little transfer occurred and termination of molecular growth was consequently largely the result of radical combination reactions. The nitrile groups in the initiator fragments, one at each end of the polystyrene molecule, provide suitable points for attachment of polyacrylonitrile blocks after treatment with Ti. Once again, it proved possible to add a roughly equal weight of polyacrylonitrile to the original polystyrene backbone.

In all these reactions it is necessary to carry out careful checks for the presence of homo-polyacrylonitrile and to prove that the structure of the final polymer is that expected from the premises described above. According to our experiments, the reactions proceed as expected with remarkable efficiency so we conclude that the Ti technique provides an extremely satisfactory route to block and graft copolymers in which acrylonitrile is the second-phase monomer.

REFERENCES