

Inter-versus Intramolecular Oligomerization of Nitrile Groups in Polyacrylonitrile

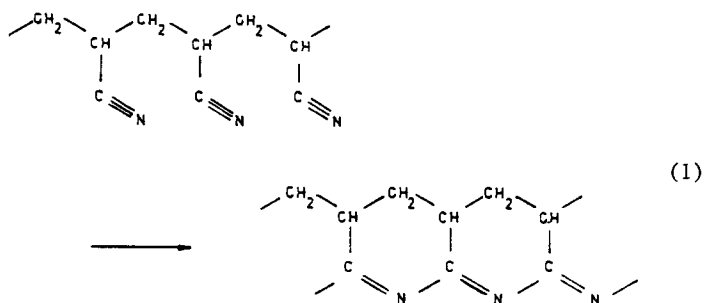
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SUMMARY

Experimental evidence is presented indicating that intermolecular oligomerization of CN groups (leading to crosslinked structures) takes place, and possibly has an even greater importance than the intramolecular reaction (leading to "ladder polymer"), at higher temperatures. The easy, quasi "built-in" crosslinking upon heat treatment is considered the most significant single feature with regard to making polyacrylonitrile and its copolymers unique among synthetic polymers as a carbon fiber precursor.

The oligomerization of nitrile groups in polyacrylonitrile (PAN) and its copolymers has been studied originally in context with the problem of thermal discoloration of these polymers (e.g. McCATHNEY, 1953; GRASSIE and McNEILL, 1958; GRASSIE and HAY, 1962). The reaction was assumed to lead to the so-called ladder structure (1), the high conjugation being one of the reasons for the color formation:



Renewed interest in the CN oligomerization reaction has emerged since fibers from PAN and its copolymers are increasingly used as precursors for carbon fibers. These precursors can be "stabilized" by a heat treatment, whereby the CN oligomerization plays

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a dominant role. (For a review, see PEEBLES, 1976.) The stabilized fibers are black, infusible and resistant to the flame. They can be further heat-treated in an inert atmosphere, to form a carbon fiber (>99% carbon). Heat treatment up to about 1400°C leads to high strength carbon fibers; with heat treatment up to about 3000°C, high modulus carbon fibers ("graphite fibers") are obtained.

The oligomerization of CN groups becomes really important at temperatures above 200°C. At such temperatures, a radical mechanism is the most probable one. The main chain carbon-carbon bonds being the weakest bonds in PAN (STEPANYAN et al., 1972), a homolytic main chain scission may safely be assumed as the first consequence of the heat treatment. The formed radicals then initiate the CN oligomerization. If uncontrolled, the exothermic oligomerization can become explosive, and the fibers may fuse. However, if a suitable temperature regime and sufficient time are provided, the stabilization proceeds smoothly.

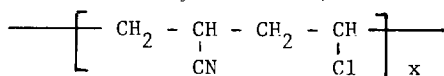
There is some controversy in the literature as to whether or not isotactic placement of acrylonitrile units in a polymer chain is necessary for the oligomerization to take place. It has even been claimed that an increase of isotacticity would enhance the rate of oligomerization (KUBASOVA et al., 1971; GEIDFRIKH et al., 1973). On the other hand, Fitzer and his co-workers (MUELLER et al., 1971) suggested, based on the shrinkage behavior of PAN during stabilization, that the presumed "ladder polymer" is in fact a "step ladder", produced by very short sequences of intramolecular reaction (1-3 steps), followed by a jump to a CN group of a different chain. We want to present experimental evidence which strongly supports this latter suggestion, and makes less probable the requirement of isotacticity.

In normal PAN, produced by a free radical process, a preponderance of isotactic sequences is not to be expected. Moreover, atom model representations of sequences of isotactic and syndiotactic placements within a PAN chain reveal that the former do not offer all that much of an advantage, if two subsequent CN groups have to be "forced" into reaction distance.

The emphasis here is on the word "forced". The mutual repulsion of adjacent CN groups in the same chain tends to hold them apart in a helix-like structure (HENRICI-OLIVE and OLIVE, 1979, and references therein). Neighboring CN groups from different polymer molecules, on the other hand, attract themselves. In fact, intermolecular dipole-dipole bonds are the main reason for the fiber forming capacity of PAN. Evidently, the strong dipole-dipole interaction between CN groups of neighboring macromolecules brings such groups into an ideal position for reaction, if a high temperature radical attack takes place (2). The consequence of this intermolecular reaction is crosslinking. This kind of arguments appears to favor the intermolecular reaction (2) over the intramolecular reaction (1).



Additional evidence for this opinion comes from differential thermal analysis (DTA) data. This method permits to observe the exothermic oligomerization reaction, under comparable conditions, for a number of different polymer compositions. Fig.1a shows the DTA exotherm, as it is usually observed with acrylic copolymers, containing mainly acrylonitrile (AN), with a few % of one or two comonomers. Fig.1b shows the DTA trace of an alternating AN/VCl copolymer (VCl = vinyl chloride):



(The copolymer has been described, and fully characterized, by WENTWORTH and SECHRIST, 1971, in another context.) This copolymer certainly does not contain isotactic sequences of AN units. Moreover, reaction of one CN group with the next in the same macromolecule is not very probable since they are too far apart. Nevertheless, there is a clear indication of the exothermic oligomerization of CN groups. The exotherm is, however, preceded in this

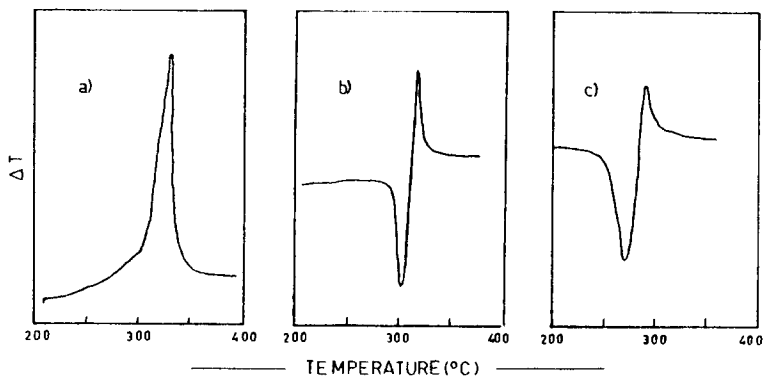
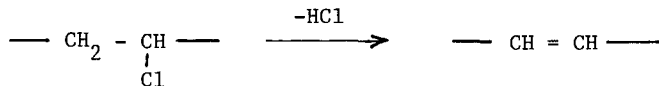


Fig.1. Demonstration of intermolecular CN oligomerization by DTA. a) AN/vinyl acetate copolymer; b) alternating AN/VCl copolymer; c) statistic 1:1 AN/VCl copolymer. Exothermic peak present in b), where intramolecular reaction is highly improbable. (Heating rate: 20°C/min.)

case by the endothermic dehydrochlorination, typical for chlorinated aliphatic compounds:



The apparent exothermic peak evidently does not account for the full amount of oligomerization taking place, since the exotherm is partly masked by the endotherm.

Fig.1c shows, for comparison, a statistic copolymer, containing AN and VCl in approximately equal amounts (commercial product). Although sequences of AN units can be assumed to be present in this case, the DTA trace is very similar to that in Fig.1b.

These data indicate that the intermolecular reaction is certainly feasible. In copolymers with larger sequences of AN units, there are possibly one or several intramolecular steps in between crosslinks. At any rate, however, extensive crosslinking takes place already in the early stages of the heat treatment. In the case of the alternating AN/VCl copolymer, where intramolecular oligomerization is not likely, the resulting $-\text{C}=\text{N}^*$ radical most probably abstracts hydrogen from any neighboring group, thus producing another R^* . The net effect of the unification of the two CN groups is then just the formation of a crosslink. Actually, an X-ray wide angle scattering investigation of heat-treated alternating AN/VCl copolymer confirms this view: we found no evidence for the "ladder" structure, as it is usually observed with heat-treated acrylic copolymers (see, e.g., UCHIDA 1971).

The behavior of polymethacrylonitrile (PMAN) fits into this picture. In contrast to PAN, PMAN is not a textile fiber forming polymer, despite the presence of the highly polar CN groups. An atom model representation of a PMAN chain shows that the CN groups are virtually buried in between methyl groups. Hence the intermolecular dipole-dipole bonds, which are so important for the properties of PAN fibers, are strongly hindered in PMAN. In accordance with this, the intermolecular CN oligomerization can not take place. In fact there is no exotherm at all to be observed (GRASSIE 1977). Evidently, the intramolecular CN oligomerization is also sterically hindered (model indicates strongly reduced rotation for the main chain C-C bonds). The only DTA feature is a broad endotherm (see Fig.2a). Since thermogravimetric analysis (TGA: see Fig.2b) reveals a nearly complete decomposition in approximately the temperature region of the DTA endotherm, the latter can confidently be assigned to depolymerization (and probably fusion), and it can be excluded that any appreciable CN oligomerization would be masked by the endotherm.

We conclude that, in PAN and its copolymers, the intermolecular CN-CN reaction is a significant contribution to the exothermic oligomerization reaction. In the resulting crosslinked structures, main chain breaks will not produce low molecular weight "fuel", thus averting excessive weight losses as well as burning and fusion. Hence, the easy, quasi"built-in" crosslinking, during the

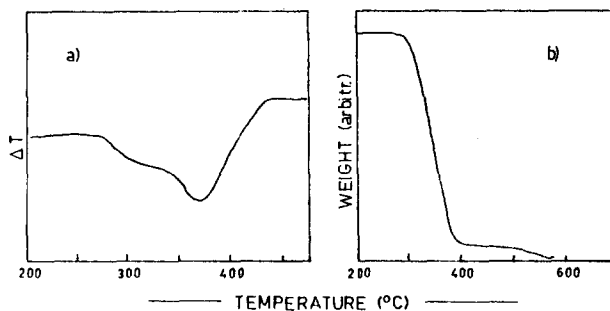


Fig.2. DTA (a) and TGA (b) of polymethacrylonitrile;
no CN oligomerization exotherm.

early stages of the stabilizing heat treatment, is probably the most important single feature with regard to making PAN and its copolymers unique among synthetic polymers as carbon fiber precursor.

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Received September 25, 1981