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# "Quick-Stabilizing" Acrylic Precursor for Carbon Fibers

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## SUMMARY

Copolymers of acrylonitrile and vinyl bromide, with ca 4% (by weight) of vinyl bromide, are used as precursors for carbon fibers. The precursor fibers can be stabilized in remarkably short time intervals (15 - 20 min), without fiber damage, and result in carbon fibers (at 1400°C) of high quality: tensile strength 3,000 MN/m$^2$, modulus 290 GN/m$^2$, density 1.7 g/cm$^3$. The chemistry behind these findings is discussed.

Polyacrylonitrile, PAN, as well as its copolymers with a few percent of a comonomer ("acrylics"), appear to be the most widely used starting materials for carbon fibers. (For a more recent review see PEEBLES, 1976.) There are two major reasons for that. On one side, stretched fibers from PAN have a high molecular orientation which can, at least in part, be maintained through the pyrolysis process, provided the fibers are continuously held under stress. This is supposed to be responsible for the high tensile strength and modulus. On the other hand, intra- and intermolecular thermal oligomerization of nitrile groups, in air at relatively low temperatures, leads to highly conjugated, crosslinked, oxidized structures, which make the fibers non-flammable and infusible. Such fibers are said to be "stabilized". They can be further heat-treated in an inert atmosphere to form "carbon fibers" ( >99% carbon). Heating to 1400 - 1600°C leads to high tensile strength carbon fibers; with heat treatment up to 3000°C, high modulus carbon fibers ("graphite fibers") are obtained.

The oligomerization of nitrile groups is exothermic (6 - 7 kcal/mol; GRASSIE,1977). As a consequence, the stabilization of the fibers must generally be carried out slowly, to avoid fiber fusion. Residence times in a stabilization furnace of 1 - 2 hours, with a carefully controlled temperature profile, are usual practice.

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We want to report on acrylic carbon fiber precursors that can be stabilized in as short a time interval as 15 - 20 min, and yet - upon the usual carbonization treatment - resulting in carbon fibers of excellent properties. The technological advantage resides in either smaller stabilization furnaces, or increased throughput.

The precursor fibers are spun from acrylonitrile/vinyl bromide copolymers (AN/VBr), with VBr concentrations in the range of 4 - 6% (by weight). Vinyl bromide features two important properties which are not found together in any other potential comonomer: a very weak bond (C-Br) which is not involved in main chain bonding, and a small molar volume.

In the absence of ionic additives, the oligomerization of CN groups during stabilization is a free radical process. The initiating radicals are formed by thermal bond breaking. In PAN and in most of its copolymers, main chain carbon-carbon bonds are the weakest bonds. In PAN, this bond has a dissociation energy of 71 kcal/mol. (This and the following bond dissociation energies are taken from STEPANYAN et al., 1972, unless otherwise stated.) Apart from radical formation, main chain bond breaking involves molecular fragmentation, and possible formation of low molecular weight fuel.

In AN/VBr copolymers, the C-Br bond is by far the weakest bond, with a dissociation energy of only 61.4 kcal/mol. During stabilization, this bond is the first to break, at a temperature significantly below that required for main chain scission, and without the fragmentation of macromolecules. Hence, the oligomerization of CN groups can start at a lower temperature than with PAN or most of its other copolymers, thus spreading the heat evolution over a greater temperature range, and preventing fiber fusion. Moreover, extensive crosslinking by intermolecular CN oligomerization (cf. HENRICI-OLIVÉ and OLIVÉ, 1981), at relatively low temperature, reduces the formation of small fragments in the temperature range of main chain scission.

As mentioned above, PAN fibers have the particular property of high molecular order (for a review see HENRICI-OLIVÉ and OLIVÉ, 1979). Vinyl bromide as a comonomer does not essentially reduce this order, due to the small volume of the bromine side chain. Since the carbon fiber tensile properties depend on orientation, the advantage is evident. Intimately related to the high molecular order is a relatively high melting point which helps to prevent fiber fusion, permitting thus stabilization at higher temperatures, as compared to other acrylic precursors. Since higher reaction temperature means increased reaction rate, there is a great potential for short stabilization time.

From the point of view of molecular order and melting point, pure PAN would appear to be the most convenient carbon fiber precursor. However, it has a number of disadvantages: no easily breaking bond; very poor oxygen permeation (SALAME,1967), taking into account that oxygen is a necessary ingredient in the further course of stabilization (see, e.g., PEEBLES, 1976; COLEMAN and PETCAVICH, 1978); moreover, pure PAN presents difficulties in wet-spinning operations which are mainly due to the high molecular order.

The advantage of small molar volume is shared by monomers like ethylene, vinyl chloride or vinyl iodide. But the first two do not have a labile bond which could give radicals before PAN main chain scission sets in (C-C in polyethylene: 84.8 kcal/mol; C-Cl in poly(vinyl chloride): 75.1 kcal/mol). Vinyl iodide, on the other hand, has too labile a bond (C-I: 53 kcal/mol, EGGER and COCKS, 1973), which probably would not even survive spinning operations.

Other monomers, such as styrene or α-methylstyrene, would provide labile C-C bonds (65.6 and 60.6 kcal/mol respectively), for early radical formation, but they involve main chain breaking; moreover, the large molar volume disturbs the molecular order. The usual comonomers for acrylic fibers, i.e. acrylates, methacrylates or vinyl acetate, do not offer any of the advantages of vinyl bromide. Hence, for several reasons, AN/VBr copolymers appear to be unique as carbon fiber precursors.

Table 1 shows the results of screening experiments with a number of acrylic polymers, under comparable conditions (not optimized). For stabilization, the fiber was slowly carried through a vertical tubular furnace of ca 6 m length, featuring a number of independently controllable heating systems which permitted to establish varying temperature profiles. The screening was carried out with profile I (for all profiles used see Table 2); the residence time in the furnace was 60 min. For carbonization, the stabilized fiber was carried through a tubular furnace of 75 cm length at 1400°C, with a residence time of 8.7 min; the fiber was held at constant length. The carbon fibers are characterized by their

Table 1. Precursor screening. (Spinning stretch 13 x; stabilization 60 min, profile I, constant length; carbonization 8.7 min, 1400°C, constant length.)

| PRECURSOR | AN / M | CARBON | FIBER PROPERTIES | |
|---|---|---|---|---|
| Comonomer M a) | Weight % M | $E_s$ (GN/m$^2$) | $\sigma$ (MN/m$^2$) | $\rho$ (g/cm$^3$) |
| VBr | 4.2 | 234 | 2200 | 1.64 |
| VBr | 5.2 | 234 | 2160 | 1.64 |
| VBr | 6.4 | 214 | 2000 | 1.61 |
| MMA | 4.4 | 214 | 1500 | 1.59 |
| MAN | 5.0 | 200 | 1400 | 1.50 |
| MA | 3.9 | 200 | 1380 | 1.68 |
| AAM | 4.0 | 200 | 1200 | 1.59 |
| VA | 4.0 | 158 | 1070 | 1.54 |
| MA/α-MSty b) | 2.0/1.9 | 158 | 1180 m | 1.60 |

a) MMA = methyl methacrylate; MAN = methacrylonitrile; MA = methyl acrylate; AAM = acrylamide; VA = vinyl acetate; α-MSty = α-methylstyrene.

b) Terpolymer

sonic modulus, $E_s$, tensile strength, $\sigma$, and density, $\rho$. The experiments in Table 1 indicate clearly the advantage of the AN/VBr precursor, with regard to carbon fiber properties.

Table 2. Temperature profiles for stabilization furnace (in degree C).

| Furnace zone \ Profile No. | I | II | III | IV |
|---|---|---|---|---|
| 1 | 260 | 260 | 260 | 260 |
| 2 | 260 → 300 | 260 → 300 | 260 → 310 | 260 → 330 |
| 3 | 300 | 300 → 330 | 310 → 330 | 330 |

Table 3 summarizes experiments carried out to shorten the stabilization time and to improve further the carbon fiber properties. These experiments were carried out with an AN/VBr fiber containing 4.2% of VBr, which had been stretched to 13 times its length during spinning; moreover, the fiber was stretched some 15% during stabilization. (This was about the maximum stretch the fiber could take in either operation.) The first run in Table 3 shows the improvement of carbon fiber properties resulting from stretching (compare with the first run in Table 1). However, with the "screening profile" I, the stabilization time could not be reduced below 40 min; at 30 min residence time in the furnace, the carbon fiber properties deteriorate (run 2 in Table 3). Other profiles, with higher final temperature, and increasing temperature gradient in the middle zone of the furnace, permitted stabilization in shorter times. Carbon fibers with very good tensile properties could be obtained with profiles II,III and IV, with stabilization times of only 15 - 20 min.

Table 3. AN/VBr Precursor: Influence of stabilization time and profile on carbon fiber properties. (4.2 % VBr; spinning stretch 13 x; stabilization stretch 15 %; carbonization as in Table 1.)

| No. | STABILIZATION |  | CARBON FIBER PROPERTIES |  |  |
|---|---|---|---|---|---|
|  | Time (min) | Profile no. | $E_s$ (GN/m$^2$) | $\sigma$ (MN/m$^2$) | $\rho$ (g/cm$^3$) |
| 1 | 40 | I | 290 | 2950 | 1.73 |
| 2 | 30 | I | 290 | 2600 | 1.72 |
| 3 | 30 | II | 290 | 3020 | 1.73 |
| 4 | 15 | II | 290 | 2950 | 1.73 |
| 5 | 20 | III | 290 | 3070 | 1.73 |
| 6 | 15 | IV | 290 | 3000 | 1.72 |
| 7 | 11 | IV | 260 | 2500 | 1.71 |

Despite the rapid stabilization, the properties of the presently reported carbon fibers compare favorably with those of most commercial high tensile strength carbon fibers (see, e.g., THORNE, 1979; SIMITZIS, 1975).

## References

COLEMAN,M.M. and PETCAVICH, R.J. (1978), J.Polym.Sci., Polym. Phys.Ed. 16, 821
EGGER,K.W. and COCKS,A.T. (1973) Helv. 56, 1516
GRASSIE,N. (1977) in GRASSIE,N. (ed.): Development in Polymer Degradation. Vol. 1, Chap. 5. Applied Science Publ., London
HENRICI-OLIVÉ,G. and OLIVÉ,S. (1979) Adv. Polym. Sci. 32, 123
HENRICI-OLIVÉ,G. and OLIVÉ,S. (1981) Polymer Bulletin 5,457
PEEBLES,L.H. (1976) in MARK,H., GAYLORD,N. and BIKALES,N. (eds.): Encyclopedia of Polymer Science and Technology. Suppl. Vol. 1. Wiley, New York
SIMITZIS,J. (1975) Ph.D. Thesis, University of Karlsruhe, West Germany
STEPANYAN,A.YE., PAPULOV,YU., KRASNOV,YE.P. and KURAKOV,G.A. (1972) Vysokomol.Soyed. A-14, 2033
THORNE,D.J. (1970) Nature 225, 1039

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