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ELECTRON-BEAM-INDUCED CYCLISATION TO OBTAIN C-FIBRE PRECURSORS FROM POLYACRYLONITRILE HOMOPOLYMERS

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Abstract—Alkyl radicals were produced and proved to be present (ESR) in polyacrylonitrile fibres which had been exposed to electron beams. By giving the irradiated fibres thermal treatment, it was possible to achieve a radical cyclisation of the PAN fibres. The mechanical textile characteristics of the fibres were determined; they were found to be suitable precursors for carbon fibres. In contrast to conventional cyclisation methods, the convenient high-energy method of irradiation does not need any external or internal catalysts (e.g. PAN copolymers), and it leads to reduced cyclisation times.

INTRODUCTION

Production processes for carbon fibres

The production technology for carbon fibres can be divided into three process levels. In the first process level, stabilisation, the PAN-fibre is heated in an oxidizing atmosphere under tension to temperatures between 200 and 300°C. In this process, the texture of the fibres must not be changed, because it is only possible to obtain anisotropic carbon fibres with layer levels which are mostly parallel to the axis of the fibre and with excellent mechanical characteristics if anisotropic, i.e. high-orientated fibres (PAN or mesophase pitch), are used to start with. The cyclisation mechanisms which take place during the stabilisation process can be ionic or radical, depending on the catalysts.

During the second process level, the carbonisation process, the fibres are heated under inert gas to about 1200–1600°C. This causes hydrogen cyanide, ammonia, water, nitrogen and other gases to separate. These compounds are formed because intermolecular elimination reactions form the ladder chain polymers of the stabilisation level into planar graphite structures.

The third process level, graphitisation, is mostly used only to produce high modulus (HM) fibres. In this process the fibres are heated up to temperatures of up to 3000°C under tension, and as a result increasingly well-ordered graphite structures are formed, and structural defects can be balanced out.

Ionic cyclisation mechanisms

According to Overhoff [1], two basic possibilities can be considered for the ionic cyclisation mechanism of the stabilisation stage: (1) the attack of a nucleophile on the C-atom of the nitrile group; or (2) the attack of an electrophile on the N-atom of the nitrile group. The preferred electrophile catalysts are both proton and Lewis acids. The practical handling of Lewis acids and a range of additional requirements often speak against using them in more applications.

In order to get around the difficulties in the application of external catalysts such as, for example, diffusing the catalyst into the fibres and later removing it, copolymers of the PAN are used. Comonomers with a catalytic effect include itaconic acid and methyl methacrylate [2–4] (see Fig. 1). Although it is known how to produce carbon fibres from these copolymers, it must be taken into consideration that the comonomers form imperfections in the PAN-polymer, which prevent the formation of a high-orientated PAN fibre structure.

Radical cyclisation mechanisms

According to Fitzer [2], two simultaneous processes determine the stabilisation process in the PAN homopolymer in the presence of the oxygen in air: the radical cyclisation of the nitrile side groups into naphthyridine sequences is hindered by the bi-radical oxygen, whilst the C-chains are partially dehydrated. Further cycling processes and oxidation processes lead to the structure shown in Fig. 2.

Grassie and McGuchan [5–7] made thorough studies of the radical mechanism. The basic thinking was that radicals can form at flawed points of the polymer when it is heated, and that these radicals (structures I–III; Fig. 3) trigger the cyclisation reactions. At points of changing tacticity, H-abstractions and re-initiation within the polymer chains can lead to a continuation of the cyclisation reaction. When this happens, the cyclic structures are interrupted by longer or shorter chains of non-cyclised units of PAN.

A problem with this mechanism is the specific thermal production of the above-mentioned radicals and with this a controllable elimination of the heat from the reaction ($\Delta H \sim -30$ to 40 kJ/mol nitrile groups between 240 and 300°C). With uncatalysed

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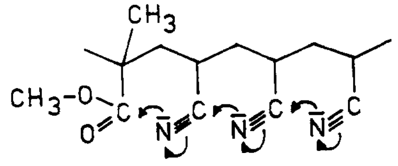


Fig. 1. Initiation of cyclisation of the PAN copolymer through the electrophile centre of the ester grouping of the methyl methacrylate.

reactions, however, this leads to durations of between 4 and 20 hr at 200–300°C [1, 8]. Currently, attempts are being made to achieve durations of under 1 hr [9–11] by using catalysis and other measures.

Electron beam irradiation as a pretreatment before stabilisation

If matter is exposed to accelerated electrons, a single-elastic collision with the shell electrons of the atoms can result. When this happens, secondary electrons ($E \leqslant$ eV) are formed. Some of the secondary electrons have such high energy ($E =$ 1–10 keV; δ-electrons) that their collisions with shell electrons can release new electrons. Most of the secondary electrons very quickly transfer their energy to the irradiated matter. As the binding energy of organic molecules (approx. 3–5 eV) is a great deal lower than that of the secondary electrons, molecular ions are generated in this process. If the amount of energy taken up by this is less than the dissociation energy, then the molecule in question passes over in an energized state:

$$AB \rightarrow AB^*.$$

The energized molecule can then pass into the ground state either by emitting light (fluorescence or phosphorescence) or by radiating heat; alternatively, it is split into free radicals:

$$AN^* \rightarrow A^\bullet + B^\bullet.$$

The irradiation tests aimed to produce these radicals; therefore, an advantage of the electron beam method is that it is possible to produce radicals in homopolymers without catalysts. A further, very important advantage is the lower energy consumption than in conventional thermic processes.

EXPERIMENTAL PROCEDURES

Electron beam production system, applied dosages and materials

With the equipment (Fig. 4) for flat materials such as textiles or fibres (max. speed ~75 m min^{-1}, dependent on beam current and dosage) which was used in this work, the electron beams were produced through the emission of electrons from a pointed glow cathode in a vacuum ($> 5 \times 10^{-5}$ hPa).

With the application of a high voltage (max. 180 kV; max. beam current 100 mA), the electrons were accelerated towards the anode and distributed by a scanner system into a surface area of 130 × 10 cm of the Lenard window. After they penetrated the thin titanium foil (12 μm) of the Lenard window, the electrons hit the specimens moved by the transparent roller (fibres or fabric). The space between the titanium foil and the samples was continually cleansed with

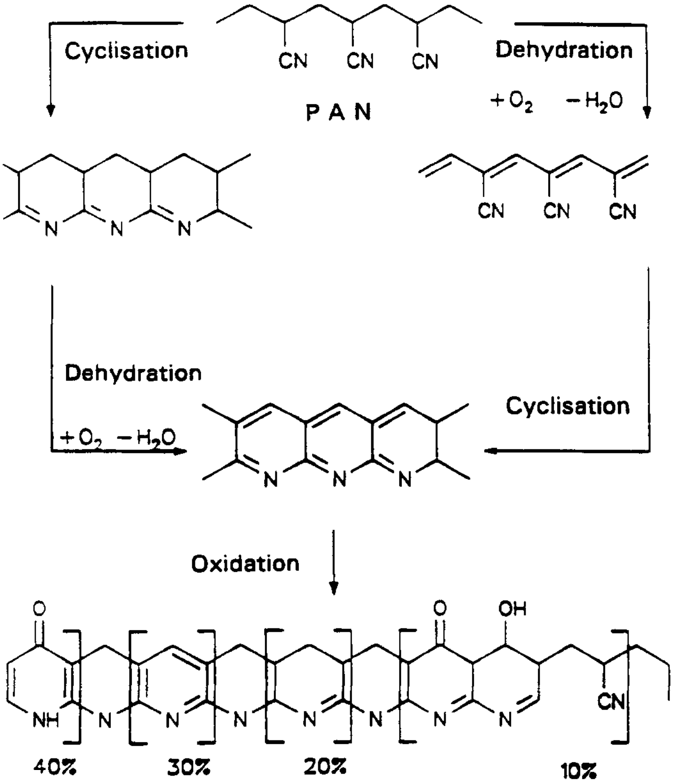


Fig. 2. Basic course of the stabilisation reaction according to Fitzer [2].

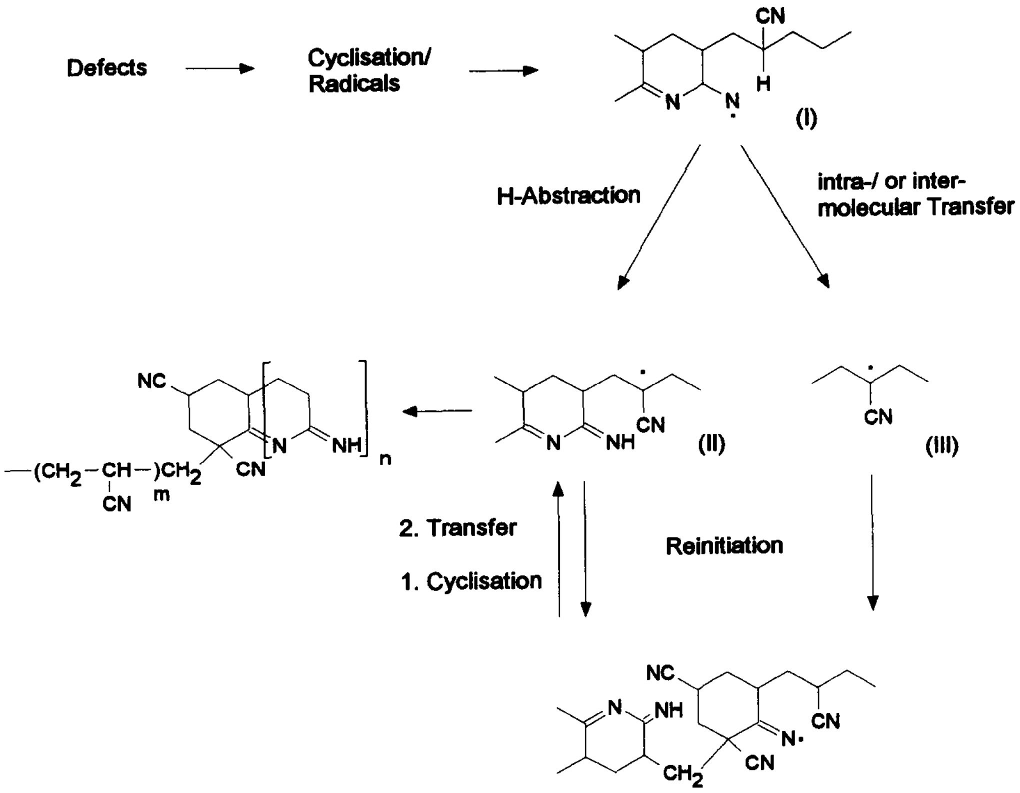


Fig. 3. Radical cyclisation mechanism according to Grassie and McGuchan [5–7].

nitrogen, and the concentration of oxygen residue was monitored. A residual oxygen concentration of 200 ppm was not exceeded. In the first stage of the process, the fibres to be irradiated were drawn into the electron accelerator by the transport roller. From previous tests, it was known that the radicals produced by the radiation treatment in the PAN homopolymers are very stable. The irradiated materials can thus be stored as required for several days until stabilisation, without any significant loss in reactivity.

The dosages of energy used in this work were between 100 and 400 Gy. The absorbed beam dosage is defined as the radiation energy absorbed per unit of mass:

$$\text{Dosage of energy} = \text{Energy/Mass}.$$

The SI unit for the dosage of energy is the Gray:

$$1\ \mathrm{Gy} = 1\ \mathrm{J\,g^{-1}}.$$

The energy dosage yield is the radiation energy absorbed per unit of time and unit of mass (SI unit = $\mathrm{Gy\ sec^{-1}}$). The dosages of energy used in this work were between 100 and 400 Gy.

The following filaments were used as PAN homopolymers: Polymer A: dtex 205/96 f30Z; Polymer B: dtex 220/96 f/non-vortical. The PAN co-polymer (methacrylate, itaconic acid) used was Polymer C: 3 K/dtex 1,22.

Stabilisation process for the irradiated fibres

A heating furnace (up to 320°C) with an extra hot air fan was used to stabilise the fibres. Two godets which were synchronised with each other (∅ ~ 150 mm, length ~500 mm, distance between them ~1000 mm) were installed inside the furnace. Owing to the fact that it was possible to set any speed setting for the godets (the settings were not restricted to a few predetermined speeds), and owing to the number of filament contacts between the godets, it was possible to set the required durations individually. By also using a supply godet it was possible to control the shrinkage of the irradiated filaments when they were being drawn into the furnace. The alignment of the godets in the furnace ensured that the reaction shrinkage could only have the effect of reducing the cross-section of the filaments.

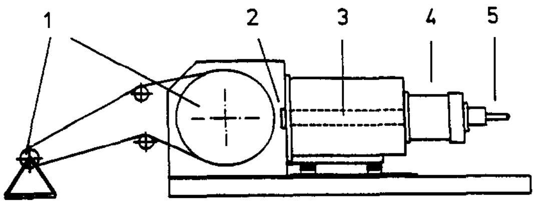


Fig. 4. Diagram of the ESH 150 electron beam equipment (Dürr Anlagenbau Company, Stuttgart; compare Zeh [12]). (1) Transport rollers with continuous belt; (2) Lenard window; (3) scanner; (4) accelerator with Wehnelt cylinder, glow cathode; (5) high-voltage cable.

RESULTS AND DISCUSSION

Effects of the electron irradiation on the PAN polymers and the cyclisation process

The electron spin resonance (ESR) test is one of the most important methods for testing materials with unpaired electrons. In this context it was of the greatest interest to use the ESR to test the type of radical produced by irradiation with accelerated electrons in PAN polymers, which as the centres of the reaction are the origin of the cyclisation. According to Bobeth *et al.* [13] and Zeppenfeld [14], two different ESR signals can appear with PAN (see Fig. 5).

When irradiation takes place in air, the ESR spectra can be assigned an alkyl radical structure if there is poor diffusion of oxygen in the fibre, or a peroxide radical structure if there is good diffusion of oxygen.

Alkyl radicals (Fig. 5) were shown to be present both in the PAN-homopolymer and in the PAN-copolymer, and their concentration increased as the beam treatment was increased (Fig. 6).

The radicals obtained are exceptionally stable and can be kept for days in an air atmosphere. There are no signs of any peroxide structures forming on the spectra.

The long-term stability of the radicals thus makes it possible to interrupt the process between the irradiation and the cyclisation of the fibres.

It can be seen from the even deepening of colour over the cross-section of the fibre after the cyclisation process that the formation of radicals has taken place over the whole cross-section of the fibre.

Even higher dosages of radiation and longer durations at even higher temperatures eventually lead to the dark-brown to black colour of the oxidised PAN. It is possible to follow the progress of the reaction by measuring the colour.

The progress of the reaction in the cyclisation can also be determined with the aromatisation index to Uchida [15]:

$$AI = I_A/(I_P + I_A),$$

where I_A is the X-ray intensity of the reflex of the aromatic structure when $2\theta = 25.5°$, and I_P is the intensity of the reflex when $2\theta = 17°$. Fink [16] gives the distance between layers of a widened graphite structure of the reflex $2\theta = 25.5°$, and assumes that this is already preformed in the stabilised PAN.

From Fig. 7, it is clear that with durations of up to 100 min no ascertainable aromatisation took place in the fibre which was not irradiated. Thus, without a catalytic pretreatment of the PAN homopolymer, it took longer to initiate radically the cyclisation to the ladder polymer. It only took 50 min to achieve an aromatisation index of 0.14. The quick increase in the aromatisation index to 0.85 over a time period of 200 min shows clearly the initiating effect of accelerated electrons on the cyclisation process.

Mechanical textile characteristics of the cyclised PAN homopolymers

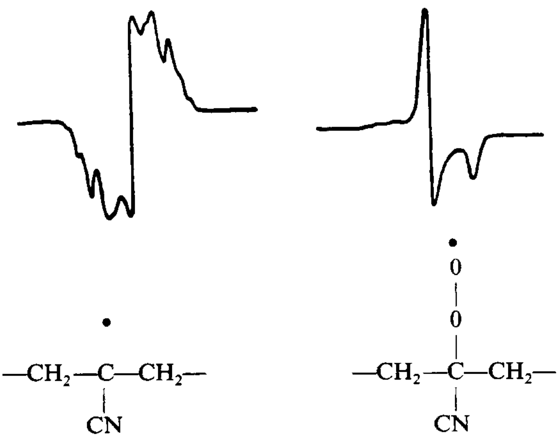
The influence of irradiation followed by cyclisation is shown in Figs 8 and 9.

With all irradiated polymers it is noticeable that there was a strong initial loss of tensile strength in comparison to the non-irradiated heat-treated fibre. The relative change in the tensile strength moved towards a limiting value, independently of the time period. The fibre which was cyclised at 250°C (time period 100 min) had the lowest tensile strength, with 180 cN/tex. This corresponds to the tensile strength of standard oxidised PAN fibres.

The irradiated polymers showed the same behaviour in the relative changes in stretch as in the relative changes in tensile strength. In line with the change in the tensile strength, the fibre has a limiting value of about 5% tear stretch at 250°C and 100 min.

CONCLUSIONS

Technical polyacrylonitrile fibres and fabrics (homopolymers) were exposed to electron irradiation and then to thermal treatment up to 300°C, in order to achieve a reduction in the time required for the stabilisation stage of the production of carbon fibres. The time periods required for stabilisation are reduced to one-third, in comparison with the traditional techniques for non-irradiated PAN fibres.



$$-CH_2-\overset{\bullet}{C}(CN)-CH_2- \qquad -CH_2-C(O-O^{\bullet})(CN)-CH_2-$$

Fig. 5. ESR spectra of PAN and PAN with peroxide structure according to Bobeth [13].

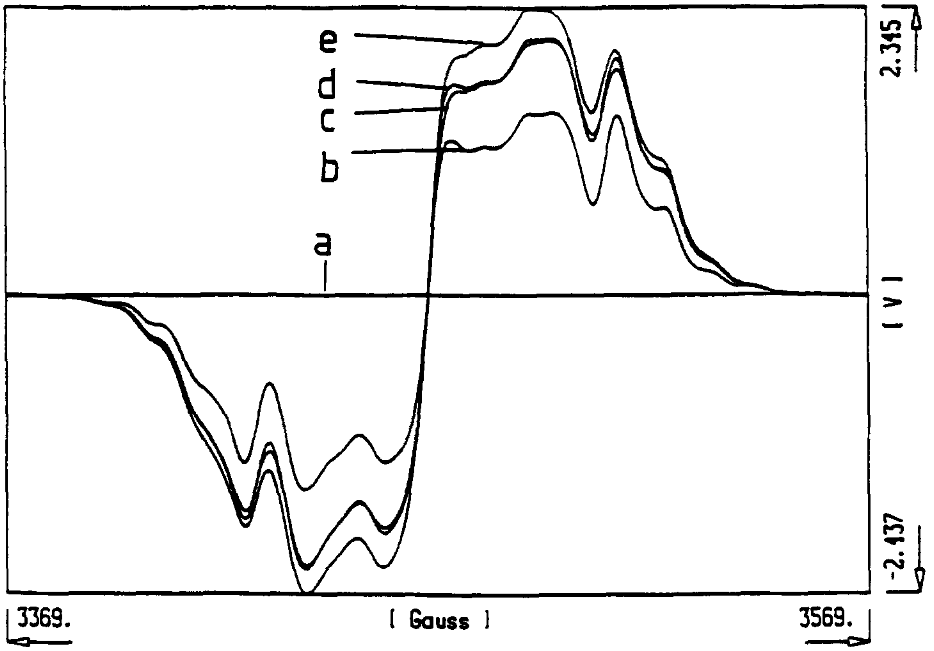


Fig. 6. ESR spectra of PAN under nitrogen, dependent on the beam dosage. (a) Not irradiated; (b) 100 kGy; (c) 200 kGy; (d) 300 kGy; (e) 400 kGy.

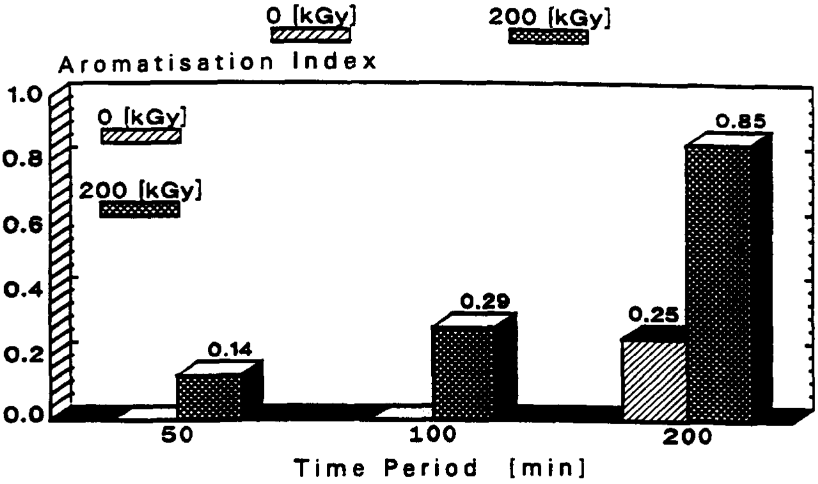


Fig. 7. Measured values of the aromatisation index according to Uchida [15].

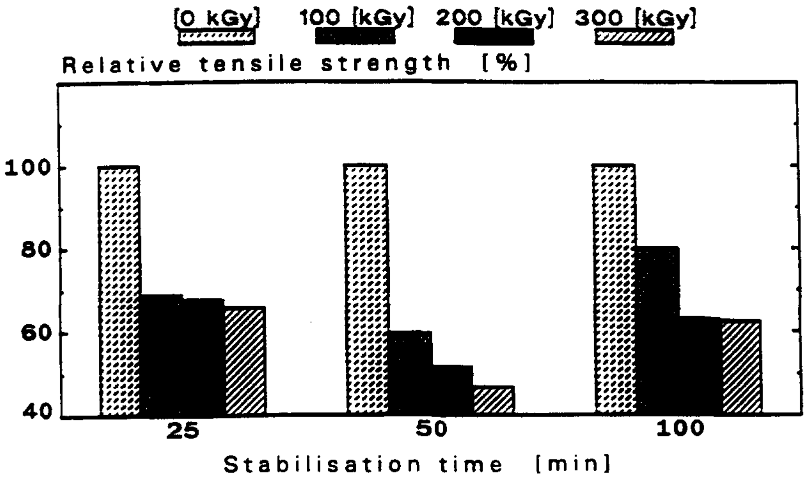


Fig. 8. Relative tensile strength of the irradiated PAN homopolymers, depending on dosage of radiation and time period at 250°C.

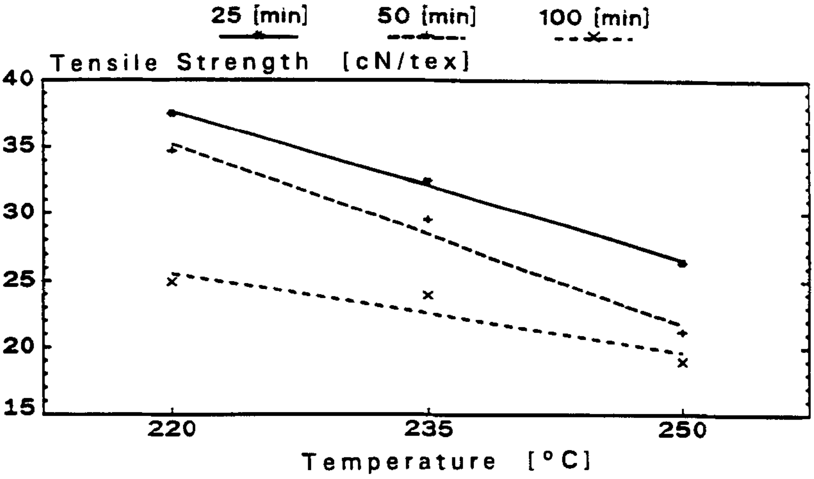


Fig. 9. Change in the tensile strength depending on the temperature and time period of PAN homopolymers with 100 kGy.

A particular advantage of the irradiation method was the stability over time of the radicals which were produced. This made it possible to have a time gap between the irradiation and the cyclisation process. Another advantage is that it is not necessary to remove any residues of catalysts from the fibres, and that the process can be used for homopolymers. The products obtained are suitable for a subsequent carbonisation process.

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