STUDY OF MOLECULAR ORIENTATION AND MOLECULAR MOTION IN HIGH
MODULE POLYAMIDE FIBRES AND MICROPLASTICS BY MEANS OF NMR

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ABSTRACT

Samples of polyamide fibres (yarns) on the basis of poly
(amide benzimidazole) (PABI) and poly(p-phenyleneterephthalate-
mine) (PPTA) have been researched by means of broad line NMR.
The same has been done as regards microplastics on the basis
of fibres PABI and epoxy resin EHD-MK and EDT-10. Orientation
and temperature dependences of the second moment of NMR
absorption line have been analysed, orientation factors of fi-
bre macromolecules and their change in plastics have been eva-
luated. It has been found that heat treatment of PABI fibres
has an influence on the orientation characteristics of NMR and
the quality of fibres and microplastics on their basis as well.

The main calculated value of NMR in fibres and plastics
being investigated is the second moment of absorption
spectrum $M^2$. Orientation dependences $M^2(\phi)$ have been treated
by the least squares according to the formula[1]:

$$M^2(\phi) = \sum_{e=0,2,4} C_e P_e(\cos \phi),$$  \quad (1)

where $C_e$ is structural coefficients, $P_e$ is Legendre's
polynomials, $\phi$ is an angle between the axis of a fibre and the
vector of a magnetic field.

Theoretical expression for $C_e$ in the model of "rigid"
lattice (That is, no molecular motions) can be given as

$$C_e = \frac{9}{2N} \delta^2 h^2 C_e P_e(\cos \psi) S_e,$$  \quad (2)

$$S_e = \sum_{d=0} r_{d}^{-6} P_e(\cos \Theta_{d})$$  \quad (3)
where $a_i$ is coefficients, $S_e$ is lattice sums, $\theta_{K}$ is an angle between the axis of fibrilla and internuclear vector $\theta_{K}$. The dash above in $P_e(\cos \psi)$ means averaging of fibrilla orientation in fibre:

$$\bar{P}_e(\cos \psi) = \int_{0}^{\pi} P_e(\cos \psi) P(\psi) \sin \psi \, d\psi,$$

$P(\psi)$ is a function of an angle distribution between the axis of a fibre and that of a fibrilla. In case of a "soft" lattice (intensive molecular motions) it is necessary to average heat motions before the operation of orientation averaging.

Heat motion averaging can be only fulfilled for concrete molecular models.

Calculation of coefficients $C_e$ for "rigid" lattice and ideal fibrilla orientations ($P_e = 1$) for intramolecular contribution (intermolecular contribution in $M_2$ is assumed to be isotrope) gives the following values (in squared oersteds, for interproton distance in aromatic rings $t_{HH} = 2.38$ Å):

- $C_0 = 2.07$;
- $C_2 = 2.56$;
- $C_4 = 4.12$ for PABI and $C_0 = 2.07$;
- $C_2 = 2.76$;
- $C_4 = 5.11$ for PPTA.

Actual fibrilla orientation is expressed by orientation factors $P_e$:

$$P_e(\cos \psi) = \frac{C_e}{C_e}(\theta_{K}),$$

where $C_e$ and $C_{e'}$ are experimental and calculated values of structural coefficients respectively. Thus, it is possible to compare the obtained parameters $P_e$ with the acoustic factor of Hermans' orientation [2]:

$$I_e = \frac{(1 - E_I/E_A)/(1 - E_I/E_K).}$$

where $E_I$, $E_A$, $E_K$ are elasticity dynamic modules of polymer isotrope and anisotrope structures respectively, and theoretical value of a particular polymer chain determined by its mechanical characteristics. For the fibres being investigated $E_I \approx 10-25$ GPa, $E_K \approx 220-240$ GPa. The results are shown in table 1. The factor $P_2$ is well agreed with the orientation parameters, obtained by means of X-ray diffraction and acoustic $I_e$.

It should be noted that the fact of twofold growth $P_4$ under heat treatment PABI is correlated with the increase of fibre strength and its dynamic module $E_A$, which can be explained supposed by improving macromolecule orientation in fibre. Unlike liquid crystals (which the fibres PPTA are also referred to), whose orientations are completely determined by factor $P_2$ (the "near" order), in fibres PABI under heat treatment, there is a structural transition, accompanied by appearing "paracrystalline" structure (the "distant" order), which is likely to be the cause of such a great change of factor $P_4$.

It has been found that for the fibres PPTA there is a convertibility of temperature dependences $M_2(T)$ and $C_2(T)$, $C_4(T)$ till the temperatures of polymer ($T \approx 400^\circ C$) destruction, which confirms the stability of their structure, formed in spinning solution.