CHEMISTRY

A. P. RUDAKOV, M. I. BESSONOV, Corresponding Member of the Academy of Sciences of the USSR M. M. KOTON,

1965

SovietRxiv

Abstract

Full Text

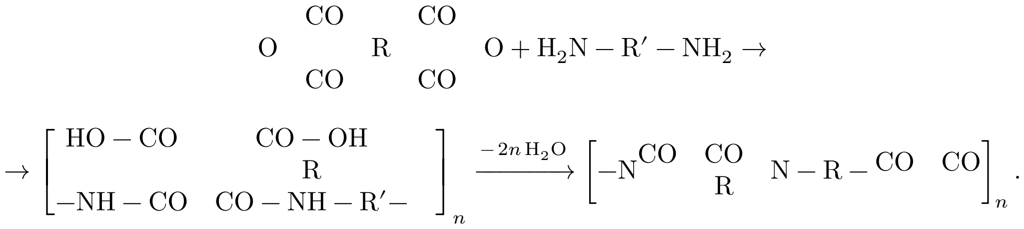
CHEMISTRY

A. P. RUDAKOV, M. I. BESSONOV, Corresponding Member of the Academy of Sciences of the USSR M. M. KOTON,
E. I. POKROVSKII, E. F. FEDOROVA

HIGH-TEMPERATURE ISOMERIC TRANSFORMATIONS

IN POLYIMIDES

The general scheme for the synthesis of polyimides (1,2) includes (1–4): (a) synthesis of a polyamic acid by condensation of a dianhydride of a tetracarboxylic acid and a diamine, and (b) dehydrocyclization of the polyamic acid to a polyimide:



$$\mathrm{O}\begin{matrix}\mathrm{CO} & & \mathrm{CO}\\ & \mathrm{R} & \\ \mathrm{CO} & & \mathrm{CO}\end{matrix}\mathrm{O} + \mathrm{H_2N - R' - NH_2} \rightarrow$$

$$\rightarrow \left[\begin{matrix}\mathrm{HO-CO} & & \mathrm{CO-OH} \\ & \mathrm{R} & \\ \mathrm{-NH-CO} & & \mathrm{CO-NH-R'-}\end{matrix}\right]_n \xrightarrow{-2n\,\mathrm{H_2O}} \left[-\mathrm{N}^{\mathrm{CO}}\begin{matrix}\mathrm{CO}\\ \mathrm{R}\end{matrix}\ \mathrm{N-R-}\mathrm{CO}\quad\mathrm{CO}\right]_n.$$

Dehydrocyclization (imidization) is carried out by thermal (3) or chemical (4) treatment of the polyamic acid.

We investigated the physical properties of polyimides at various stages of heat treatment. The dianhydrides used were: pyromellitic acid dianhydride (DAPK), diphenyltetracarboxylic acid dianhydride (DAFK), and an aliphatic tetracarboxylic acid dianhydride (DAAK). The diamines used were: diaminodiphenyl ether (DADFE) and benzidine (BN). Polycondensation was carried out in dimethylformamide at +15°. Films of polyamic acids cast from solution were dried and subjected to heat treatment, during which the following were recorded: sample weight, strength, modulus of elasticity, elongation at break, dielectric-loss tangent, and IR absorption spectra.

Table 1

Temperature, °CTime, min	Air	Air	Air	Vacuum 10^{-3}	Vacuum 10^{-3}	Vacuum 10^{-3}
Temperature, °C	+40	+80	+130	+200	+300	+400
Time, min	120—240	30	30	30	30	30

Table 1 gives typical regimes of heat treatment for aromatic polymers. Treatment of aliphatic polymers was completed at lower temperatures.

On the basis of a number of independent indicators, it may be stated that imidization according to the scheme given is largely completed already at +200°. Indeed, after heating at +200° the weight of the polymer (DAPK + DADFE system) becomes equal to the weight of the dianhydride and diamine taken mole for mole, after subtracting the weight of an equimolar amount of water. For all systems, the dielectric-loss tangent after +200° drops sharply and subsequently changes only slightly (Fig. 1a). The absorption coefficient at the 3280 cm^{-1} band of the IR spectra, which corresponds to stretching vibrations of amide groups, also decreases sharply after heating at +200° (Fig. 1b). These observations are readily explained by replacement of amide and hydroxyl groups by imide groups. In recording the IR spectra at⋯

During continuous heating of the films at a rate of 5°/min, it could be observed that the band at 3280 cm^{-1} disappears completely at +250°.

Thus, taking time effects into account, it may be asserted that the intensive development and completion of the imidization reaction occur at $+200 \div +250°$.

However, heating polyimides at higher temperatures leads to further transformations that do not fit into the scheme indicated. Moreover, in many cases only after heating up to +400° can one expect to obtain high-quality films. Indeed, from Fig. 2, which illustrates the change in the mechanical properties of DAPK + DADPE films during their heat treatment, it is evident that after heating at +200° and completion of imidization the elasticity decreases substantially. This can be explained by the formation of rigid intramolecular imide rings. However, subsequent heating at +300 and +400° leads to a sharp increase in elasticity: the elongation at break increases by a factor of 8-10. This unexpected effect is difficult to associate, for example, with thermodestruction processes, which, as a rule, lead to a decrease in elasticity and, for the DAPK + DADPE system, occur in general only at high temperatures ([5]). Its nature could be judged from changes in the mechanical characteristics. It was found, for example, that the elastic modulus increases monotonically both during the imidization process, when its growth is readily explained by cyclization, and at high temperatures (Fig. 3). This also leads to the fact that the direct and reverse temperature courses of the elastic modulus of polyimide films whose imidization had been

Fig. 1

Figure 1: Fig. 1

Fig. 2 and Fig. 3 graphs

Figure 2: Fig. 2 and Fig. 3 graphs

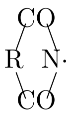
completed beforehand do not coincide. In the high-temperature region, the elastic modulus on the reverse course always has higher values than on the direct course.

Fig. 1. *a*—change in $\tan\delta$ (50 kc, 20°) after heat treatment of DAPK + DADPE (1) and DAPK + BN (2) films. For DAPK + DADPE at +200°, $\tan\delta$ was measured after 5 and 30 min of heating; *b*—change in the absorption coefficient of the 3280 (1) and 1780 cm^{-1} (2) bands in the IR spectra after heat treatment of DAPK + DADPE films.

Such changes in the elastic modulus in polymers may be associated either with crystallization or with spatial structuring—the formation of an intermolecular network. From X-ray diffraction patterns it was possible to determine that crystallization did not occur in our case. On the contrary, in favor of structuring, in addition to the elastic-modulus measurements, other, more direct experiments also testified. It turned out, for example, that if an imidized DAPK + DADPE film is stretched at +320 ÷ +340° (stretching is possible by a factor of 1.5-2) and heated in the stretched state at +400°, then afterward it is not possible to "remove" the orientation of the film. No matter to what temperatures it is heated in the free state, its dimensions remain unchanged. Conversely, if drawing is carried out at room temperature, then the initial dimensions of the film are completely restored upon heating. Obviously, in the first case the intermolecular net—

fixes the macromolecules in an oriented state. At normal temperatures, the network does not arise. This effect—the combination of orientational "hot" drawing with spatial structuring—can be used to obtain shrinkage-free fibers.

Since the phenomena described were observed for all the polyimides studied, it may be assumed that high-temperature structuring is associated with the presence of imide rings

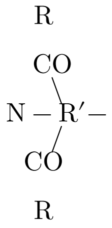


Obviously, the basis of the structuring is the reversible rupture of CO—N bonds and their recombination.

Fig. 2. Change in strength and elongation at rupture (measured at 20°) after heat treatment of DAPK + DADFE films.

Fig. 3. Change in the static modulus of elasticity of DAPK + DADFE films with time at different temperatures. Medium—argon.

The latter may end not only in the formation of intramolecular rings, but also in interchain bonds of the type



Direct evidence of decyclization is the decrease in intensity of the 1780 cm^{-1} band in the IR spectra, assigned to stretching vibrations of $C = O$ bonds in five-membered rings after heating at +300 and +400° (Fig. 1b), and A. Boldyrev' s detection of stable N radicals in high concentrations in heat-treated polyimides.

The process we have studied is, in fact, an isomeric transformation in macromolecules, occurring not only within one chain but also involving neighboring chains. Apparently, such transformations can be used to control the properties of other heat-resistant polymers as well.

Institute of High-Molecular Compounds
Academy of Sciences of the USSR

Received
5 XI 1964

CITED LITERATURE

1. *Plast. Techn.*, **8**, No. 12, 26 (1962).
2. L. Amlorski, *Ind. and Eng. Chem., Prod. Res. Dev.*, **2**, No. 3, 189 (1963).
3. G. Bower, L. Frost, *J. Polym. Sci.*, **A1**, No. 10, 3135 (1963).
4. L. Frost, J. Kesse, *J. Appl. Polym. Sci.*, **8**, No. 3, 1039 (1964).
5. S. Nishizaki, A. Fukami, *J. Chem. Soc. Japan, Ind. Chem. Sec.*, **67**, No. 3, 474 (1964).

Note: Figure translations are in progress. See original paper for figures.