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Abstract

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FREE-RADICAL POLYMERIZATION OF TRIAZINE RINGS

A necessary condition for the occurrence of the polymerization process is a decrease in the free energy of the system, $\Delta F = \Delta H - T\Delta S$, upon addition of a monomer molecule to a free radical. Since during polymerization the entropy of the system S always decreases, in order to decrease the free energy F it is necessary that the heat content of the system also decrease. In most cases the quantity ΔH is determined by the difference between the energies of the bonds formed and broken (the change in heat content as a result of a change in the character of intermolecular interaction usually plays an insignificant role). However, if in the course of polymerization the polymer, together with the growing polymer radicals, precipitates, the role of polymer-polymer intermolecular interaction may increase substantially; this will lead to a decrease in the heat content in the final state and, consequently, to a decrease in its free energy. In this case, apparently, polymerization may become possible for monomers for which the absolute value of ΔH, calculated simply from bond energies, is less than the absolute value of $T\Delta S$.

To test this assumption, an investigation was carried out of the free-radical polymerization of substituted triazines whose heat effect of polymerization, calculated from bond energies, should be close to zero (or even negative), while the polymer formed, representing a polyene chain with conjugated double bonds $(\mathrm{C=N})_x$, does not melt up to very high temperatures.

The experiments performed showed that, when substituted triazines with electron-withdrawing substituents (CCl_3, CF_3, C_3F_7) and trifluoroacetic acid nitrile are heated in the presence of a source of free radicals (azomethane and azoethane) at 250–300°C, black infusible powders are formed. In the absence of an initiator, analogous products are formed when substituted triazines are heated at 500°C. Triazines with electron-donating substituents (CH_3) do not polymerize under the indicated conditions, which is apparently connected with the very high stability of symmetric triazines with electron-donating substituents. However, under more severe conditions (heating with the radical source CF_3, perfluoroacetone, at 520°C), polymers are also formed from this compound.

The products obtained were investigated spectroscopically and by the EPR method. The UV spectra of these products show intense continuous absorption up to 500–600 mμ, which indicates the presence of a strongly conjugated

Fig. 1. IR spectra

Figure 1: Fig. 1. IR spectra

system of double bonds. In the IR spectra of all the products studied, a broad absorption band is observed with a maximum in the region 1630-1640 cm^{-1}. This band is attributed to stretching vibrations of the $C = N$ double bonds in the conjugated system. Its position coincides with that of analogous bands in the spectra of polyacetonitrile and of the polymers $(CF_3CN)_x$ and $(CHF_2CN)_x$, samples of which were kindly supplied by Moscow University.

Figure 1 gives the IR spectra of some products and of polyacetonitrile, in which the absorption band at 1580 cm^{-1}, assigned to vibrations of the triazine ring, is absent; intense bands are observed in the regions 1000–1200 cm^{-1} and 700–800 cm^{-1}, caused by vibra-

with C—F bonds, which is especially interesting in the case of the polymerization product of 2,4,6-trimethyl-1,3,5-triazine (Fig. 1, *III*) in the presence of CF_3 radicals. This indicates that the reaction of peralkylation of the triazine rings proceeds by a free-radical mechanism. This is also confirmed by the appearance of bands of C—H stretching vibrations in the region 2800–3000 cm^{-1} in the polymerization products of fluorinated triazines with CH_3 and C_2H_5 radicals (Fig. 1, *Ia*, *b*, *IIa*).

Fig. 1. IR spectra of the polymer from tris-2,4,6-trifluoromethyl-1,3,5-triazine, obtained with nitrogen at 280°C (*Ia*), washed in NH_3 (*Ib*), and obtained at 500°C without initiator (*Iv*); of the polymer from tris-2,4,6-perfluoropropyl-1,3,5-triazine, obtained with nitrogen at 280°C (*IIa*), obtained at 490°C without initiator (*IIb*); of the polymer from trifluoroacetonitrile, obtained with nitrogen at 280°C (*IIv*); of the polymer from 2,4,6-trimethyl-1,3,5-triazine, obtained with hexafluoroacetone at 520°C (*III*); polyacetonitrile (*IV*).

In all the IR spectra, moreover, an absorption band is observed at 1410 cm^{-1} and a broad absorption band in the region 3100-3200 cm^{-1}. The first is due to H—F vibrations in the HF_2^- ion, formed on heating; the second, to N—H vibrations in the $N—H^+$ group, formed by the proton H^+ and the unshared pair of electrons of nitrogen. Both of these bands disappear after washing the products with concentrated ammonia (Fig. 1, *Ib*).

The absorption bands in the region of 3400 cm^{-1} are caused by traces of moisture in the KBr pellets, into which the samples were pressed at a pressure of 100 atm. The UV spectra of the products were studied on an SF-4 spectrophotometer in sulfuric acid solution, and the IR spectra on a UR-10 double-beam spectrophotometer in KBr pellets with product weights from 0.3 to 1 mg.

The EPR spectra are identical for all samples and differ only in intensity. Lowering the temperature to 77°K does not lead to a change in the width of the EPR line, but is accompanied by a strong increase in intensity. A typical absorption line is shown in Fig. 2, from which it is seen that the EPR spectrum is a single symmetrical singlet without hyperfine structure, with a g-factor of 2.003; the width between the points of maximum slope is 8–18 oersteds for different samples.

The narrowness of the EPR signals and the absence of hyperfine structure indicate a high degree of delocalization of the unpaired electrons over the ···

polymer chain. The concentration of paramagnetic particles per 1 g for polymers from tris-(trichloromethyl)- and tris-(trifluoromethyl)-2,4,6-triazines is, respectively, $6 \cdot 10^{16}$ and $1.1 \cdot 10^{17}$. As was to be expected, the polymer from triazine with electropositive substituents (trimethyltriazine) showed a very high concentration of paramagnetic particles ($8 \cdot 10^{18}$).

E.p.r. spectra were recorded at 20 and $-190°$ on an EPR-2IKhF spectrometer with high-frequency modulation of the magnetic field (sensitivity 10^{14} spins per 1 g). To determine the absolute spin concentration, single crystals of $CuCl_2 \cdot 2H_2O$, containing a known number of paramagnetic ions, were used. The signal intensity was determined by double integration of the derivative of the absorption line. The spectral data and e.p.r. spectra give grounds to believe that these products are polyene polymers with a conjugated system of bonds $(C = N)_x$.

Free-radical polymerization of triazine rings, which apparently consists in the addition of a free radical (low-molecular or polymeric) to the ring at the double bond, followed by opening of the ring,

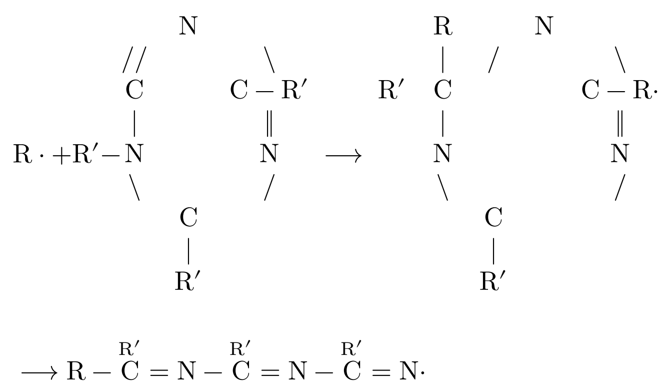

Fig. 2. E.p.r. spectrum of polymerization products of substituted triazines

at a sufficiently high temperature must be accompanied by a depolymerization reaction—the cleavage of monomeric units from the polymer radical (in the present case, the corresponding nitriles). Chromatographic analysis of the gaseous products formed during the polymerization of triazines showed that an appreciable amount of nitriles is obtained only when the reaction is carried out above 500°C. Thus, a noticeable shift of the "polymer radical—monomer" equilibrium toward the monomer occurs only at temperatures above 500°C. The limiting temperature for the "free radical—nitrile" system lies in the region of very high temperatures, in all probability as a consequence of the extremely strong intermolecular interaction between chains.

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