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Abstract

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THE CAGE EFFECT AND THE THERMOSTABILITY OF POLYMERS

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There exists a large number of organic substances whose thermal stability in solution or in the melt is considerably lower than in the solid state. Most typical in this respect are various compounds containing labile bonds (peroxides, azo and diazo compounds), which begin to decompose only at the temperature of their melting. At the same time, the thermal decomposition of these substances in solution proceeds at a considerable rate at a much lower temperature (see Table 1).

Table 1

Thermal stability of some compounds in the solid state and in solution

Compound	Formula	M.p., °C	Temp. of thermal decomp. in solution, °C	Source
Azisobutyric acid dinitrile	$(CH_3)_2C(CN)-N=N-C(CN)(CH_3)_2$	104 (with decomp.)	70–80	(1)
Benzoyl peroxide	$C_6H_5COOCC_6H_5$ ‖ ‖ O O	103.5	60–70	(2)
p-Nitrobenzoyl peroxide	$n-NO_2C_6H_4COOOCC_6H_4NO_2$ ‖ ‖ O O	158	80	(3)
4,4-Bisbenzoldiazoaminobiphenyl	$C_6H_5-N=N-NHC_6H_5C_6H_3-N=N-NHC_6H_5$	130	135	Our data

Compound	Formula	M.p., °C	Temp. of thermal decomp. in solution, °C	Source
Benzaldehyde diperoxide	cyclic peroxide structure, with two C_6H_5CH groups and two O—O bonds	200 » »	No data	(4)
Benzophenone diperoxide	cyclic peroxide structure, with $(C_6H_5)_2C$ and $C(C_6H_5)$ groups and two O—O bonds	212.5 » »	No data	

The experimental data presented below make it possible, as it seems to us, to connect this phenomenon with a sharp increase in the role of the cage effect (reactions of primary recombination of free radicals) in viscous and solid media.

As was shown earlier, the thermal decomposition of methylphenyltriazene in a hydrocarbon medium leads to the formation of methane and methylaniline (5):

$$CH_3{-}N{=}N{-}NHC_6H_5 \longrightarrow \begin{cases} CH_4, \\ CH_3NHC_6H_5 \end{cases}$$

It is most probable that methylaniline is formed as a result of recombination of radicals formed at the moment of decomposition in the "cage." This follows

from the fact that the yield of alkylanilines in the decomposition of various fatty-aromatic triazenes is practically independent of the reactivity of the alkyl free radicals formed as a result of triazene decomposition (5). In addition, the formation of methylaniline through recombination acts outside the cage does not appear possible because of the high activity of the methyl radical in the reaction of interaction with isopropylbenzene.

Table 2

Yield of the principal products of transformation of free radicals in the decomposition of methylphenyltriazene in various media. Triazene concentration 10%. Temperature 110°

Polymer content in isopropylbenzene, wt. %: polyisobutylene	Polymer content in isopropylbenzene, wt. %: polystyrene	Yield, % of theory: CH_4	Yield, % of theory: $CH_3NHC_6H_5$
–	–	49.0	15.0
5	–	47.5	Not determined
50	–	35.5	Not determined
66	–	27.0	Not determined
–	5	45.0	Not determined
–	50	28.0	Not determined
–	90	9.5	43.5

We have established that, when the decomposition of methylphenyltriazene is carried out in hydrocarbon–polymer systems, the yield of methane decreases with increasing viscosity of the medium. At the same time, as was shown for the polystyrene–cumene system, the yield of the product of primary recombination, namely methylaniline, increases (see Table 2).

The conclusion that the decrease in the methane yield is associated with an increase in viscosity, and not with a decrease in the amount of isopropylbenzene, is confirmed by the following data. We have shown that, at equal weight concentrations of different samples of polystyrene in isopropylbenzene, the methane yield is the lower, the higher the molecular weight of the polymer (see Table 3).

Table 3

Effect of the molecular weight of the polymer on the methane yield in the decomposition of methylphenyltriazene

Polystyrene content in isopropylbenzene, wt. %	Molecular weight of polymer	Yield of CH_4, % of theory
66	600 000	20
66	200 000	30

The data presented indicate a substantial influence of the viscosity of the medium on the effectiveness of the interaction proceeding in the cage. The results of the present work make it possible to consider the question of the possible influence of the aggregate state on the thermal stability of substances containing labile bonds (see Table 1), as well as of polymers that possess a

high softening temperature. The difference in the behavior of compounds of this kind in the solid state and in solution (or in the melt) can be explained by the especially great role of the cage effect in the solid state. Consideration of facts concerning the thermal stability of high-melting polymers makes this conclusion especially convincing.

As is known, poly-p-xylylene,

$$\sim CH_2C_6H_4CH_2CH_2C_6H_4CH_2 \sim,$$

whose melting temperature reaches 425°, decomposes only after passing into the molten state. In solution this polymer undergoes considerable decomposition already at 302° (6). There are a number of other polymers that have a high melting temperature and are stable up to the point at which the melting point is reached, for example:

$$\sim CH_2CH_2OC\,C_6H_4C{=}CC_6H_4COCH_2CH_2 \sim$$
$$\begin{matrix} \| & \| \\ O & O \end{matrix}$$

m.p. 420° (with decomposition)

$$\sim NH(CH_2)_6NHCOC_6H_4CO \sim$$

m.p. 350° (with decomposition)

Obviously, we are dealing here with "overheated" polymers, which begin to undergo destructive decomposition only after passing through the glass-transition temperature, when the viscosity of the system drops sharply. It may be assumed that in rigid systems (below T_g, or below the melting temperature for crystalline polymers) the primary thermal acts of rupture of C–C bonds do not cause depolymerization, precisely because of the cage effect, which returns the system to its initial state. Only the transition into the elastic region creates the conditions for the destruction process, which is manifested in the sharp drop in the thermal stability of polymers above their softening or melting temperature.

On the basis of the considerations set forth, it should be accepted that the thermal stability of polymers characterized by a high melting temperature must undergo sharp jumps in the transition from the solid state to the elastic state and from the elastic state to solution.

In the latter case, the thermal stability of the polymer is determined by the strength of the skeletal bonds of the polymer chain. The fact mentioned above, indicating a decrease in the thermal stability of polyparaxylylene in solution, speaks in favor of this point of view.

On the basis of these ideas one may conclude that the task of increasing the thermal stability of carbon-chain polymers in the glassy state is reduced above all to the need to raise their melting temperature. For rubber-like polymers, in which the cage effect is manifested to a lesser degree, high thermal stability can apparently be achieved only through the strength of the skeletal bonds of the main chain.

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