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Synthesis and Properties of Copolymers Having Polyconjugated Blocks in the Macromolecules. III. Thermal Behavior of Polyisoprene-Containing Polyazophenylene Fragments in the Main Chains*

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ABSTRACT

The thermal and thermooxidative stability of polyisoprene containing polyazophenylene fragments of different composition was investigated. Elevated inhibiting activity of polyazophenylene-methane fragments was found to be caused by the intramolecular synergism due to the combination of the reaction of peroxy radicals with mobile hydrogen atoms of methylene bridge groups and decomposition of hydroperoxides under the influence of polyconjugated blocks.

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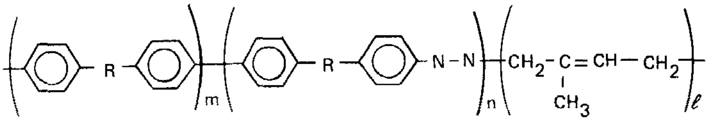
*This paper is dedicated to the memory of A. A. Berlin.
†Deceased.

In the previous part of this series [1] we described the use of aromatic N,N'-bis(nitrosoacetyl)diamines for the synthesis of copolymers with different contents of polyconjugated blocks in the macromolecules. This paper represents the results showing the peculiarities of the thermal behavor of polyisoprene containing polyconjugated polyazophenylene fragments in the main chain of macromolecules:



where R may be - (BI); $-O-$ (EI); $-CH_2-$ (MI); or $-SO_2-$ (SI). Such copolymers have some specific properties caused by the enhanced intermolecular interaction of polyconjugated blocks. They give a narrow EPR signal corresponding to a content of paramagnetic centers of 10^{16}-10^{17} spins/g. They have an absorption maximum at 530-560 nm, while polyazophenylenes synthesized under the same conditions demonstrate an absorption maximum at 360-380 nm. The viscosity curves (inherent viscosity vs. concentration) of dilute copolymer solutions are anomalous, the maximum corresponding to concentrations of 0.2-0.4 g/dl. These peculiarities have been explained by the formation of polyazophenylene blocks which partially dissociate with dilution of the copolymer solutions.

Further investigations showed that the association has a profound influence on the thermomechanical properties of copolymers. It is seen from Fig. 1 that polyisoprene with intrinsic viscosity of 0.35 dl/g has a temperature of viscous flow at -40°C while copolymer BI-11 (figure denotes the weight content of polyazophenylene fragment) with intrinsic viscosity of 0.30 dl/g has a plateau of high elastic deformation and a temperature of viscous flow at approximately 60°C. The introduction of methyl side groups into the benzene rings of polyazophenylene fragments reduces the packing of associates. Hence new elastoplastic materials in which high energies of interaction between polyconjugated blocks provide physical vulcanization can be obtained from copolymers containing elastomeric and polyazophenylene blocks.

It was shown earlier [2] that the inhibiting action of polyconjugated polyazophenylene fragments of BI copolymers in the process of thermal oxidation is considerably higher than that of polyazophenylene mechanically mixed with polyisoprene. In a previous paper in this series [1] we demonstrated that the introduction of bridge groups into polyazophenylene fragments has a small influence on the effective degree of conjugation. We therefore could expect that bridge groups would not change the inhibiting activity of polyazophenylene fragments. A kinetic study of thermal oxidation of copolymers *BI*, *EI*, *SI*, and *MI* showed that polyazophenylene fragments with methylene groups are

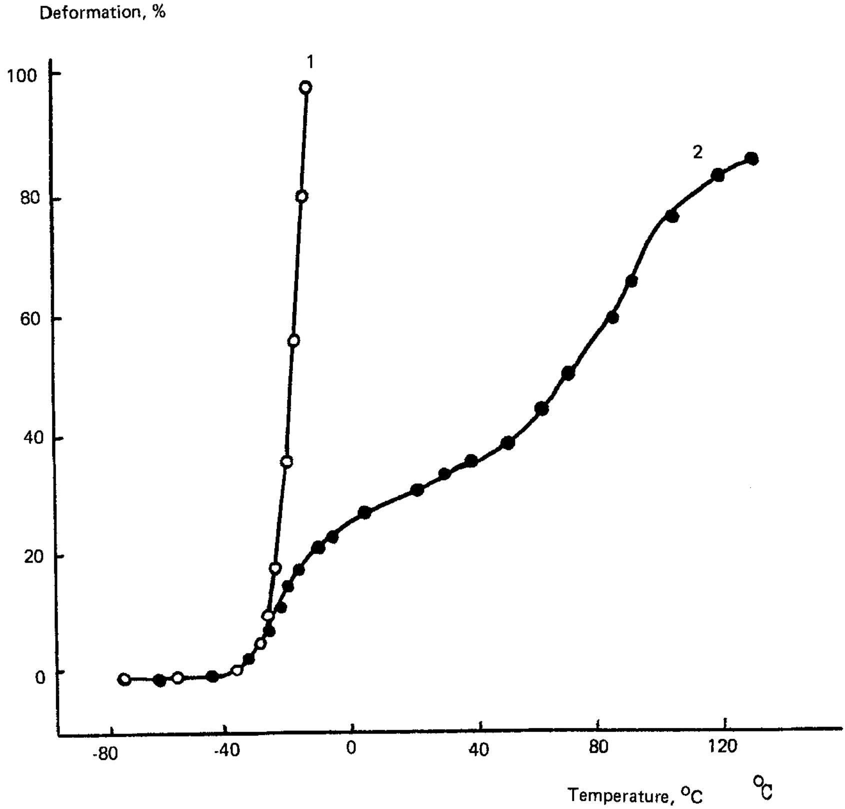


FIG. 1. Thermomechanical curves of (1) PI and (2) BI-11. Load, 1.6 kg/cm^2; heating rate, 200°C/hr.

the most active in inhibiting thermal oxidation (Figs. 2 and 3). This phenomenon can be explained by elevated inhibiting activity of methylene bridge groups possessing mobile hydrogen atoms in the reaction with peroxy radicals:

Oxygen addition to this radical and subsequent hydrogen abstraction lead to the formation of hydroperoxide which decomposes giving inactive products [3]

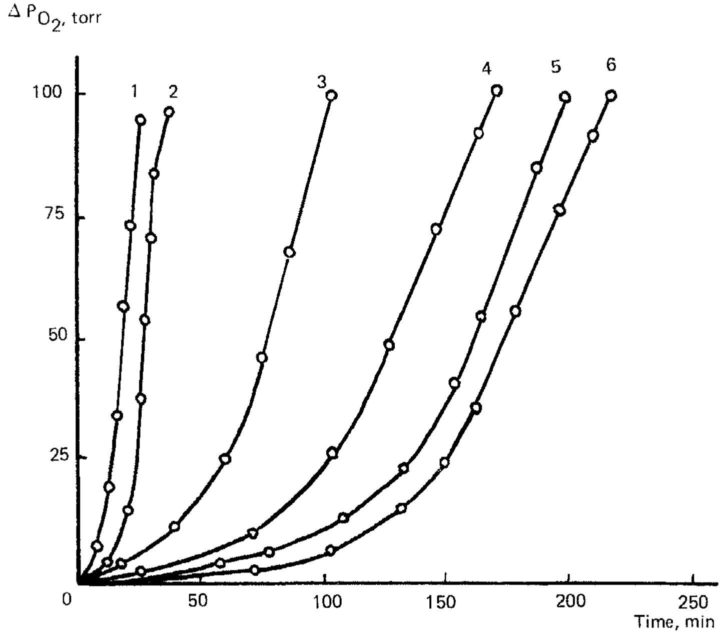
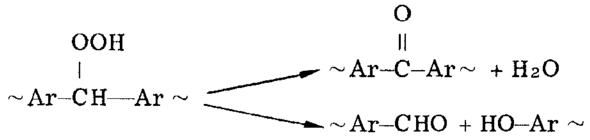


FIG. 2. Oxygen absorption curves: (1) PI; (2) PI + 5% PAF-M; (3) EI-3; (4) BI-11; (5) MI-3; (6) SI-15. Temperature, 140°C; initial oxygen pressure, 760 Torr.



$$\sim\mathrm{Ar{-}\overset{\displaystyle OOH}{\overset{|}{C}H}{-}Ar}\sim \;\begin{cases} \longrightarrow \sim\mathrm{Ar{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}Ar}\sim + H_2O \\ \longrightarrow \sim\mathrm{Ar{-}CHO} + \mathrm{HO{-}Ar}\sim \end{cases}$$

Thus the inhibiting effect of methylene bridge groups can ensure the increase of induction periods on oxidation of MI copolymers as compared with BI, EI, and SI copolymers.

It is known [4] that the mixtures of inhibitors deactivating peroxide radicals with inhibitors decomposing hydroperoxides give synergistic effects in processes of thermal oxidation; this phenomenon is also observed in the case of antioxidants of high molecular weight [5]. If the inhibiting action of MI copolymers is due only to the abstraction of mobile hydrogen atoms, there must be a synergistic effect with sulfur-containing substances for decomposition of hydroperoxides.

We attempted to enhance the inhibiting effect of polyazophenylene fragments of MI copolymers by the addition of dilauryl thiodipropionate (DLTP) which is known to decompose hydroperoxides [6]. From the results of thermal oxidation of DLTP-MI mixtures (Fig. 4)

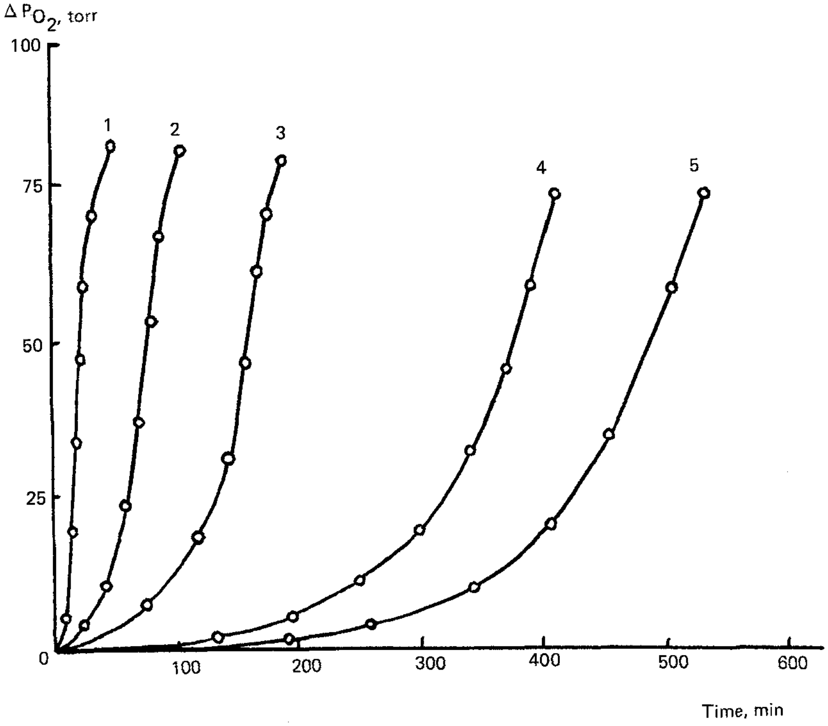


FIG. 3. Oxygen absorption curves: (1) PI; (2) MI-2,5; (3) MI-3; (4) MI-5.5; (5) MI-6.4. Temperature, 140°C; initial oxygen pressure, 760 Torr.

one can see that DLTP causes only an additive increase of the induction period. We thus conclude that organic sulfides do not influence the process of decomposition of hydroperoxides in the presence of MI copolymers because a more active decomposer of hydroperoxides is present in the system.

It is known [7] that small quantities of polyconjugated compounds can considerably increase the rate of decomposition of hydroperoxides with the formation of inactive products. Apparently the same effect takes place in the case of copolymers consisting of polyisoprene and polyazophenylene blocks. Combination of this process with the interaction of peroxy radicals with methylene groups of polyazophenylene fragments of MI copolymers provides effective inhibition of oxidation of polyisoprene blocks. In other words, intramolecular synergism in this case is as effective as in the case of the mixtures of inhibitors having a different mechanism of action.

Dynamic thermogravimetric analysis of BI copolymers containing

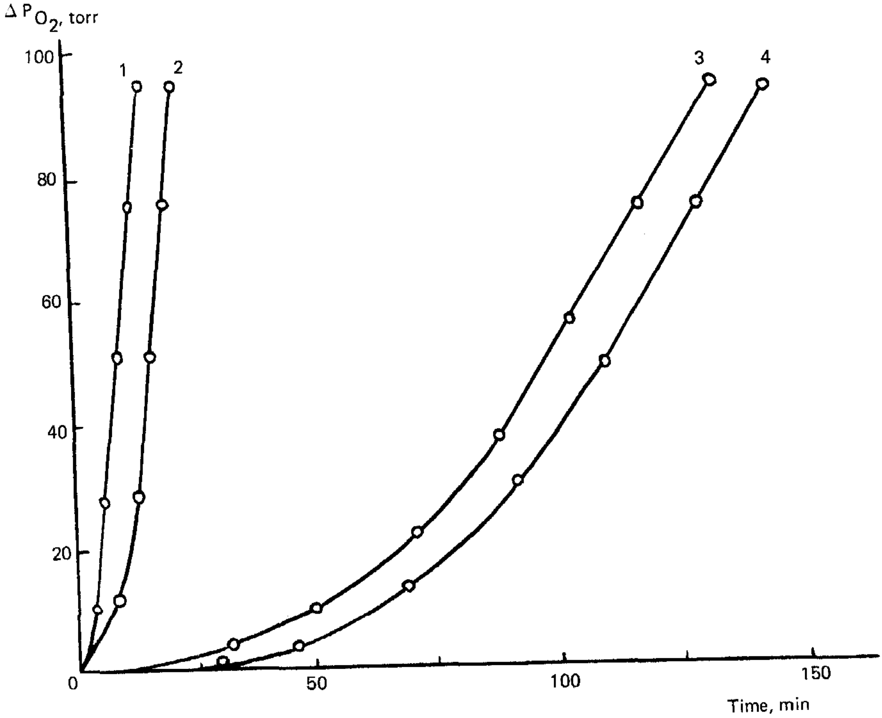


FIG. 4. Oxygen absorption curves: (1) PI; (2) PI + 1% DLTP; (3) MI-4; (4) MI-4 + 1% DLTDP. Temperature, 140°C; initial oxygen pressure, 760 Torr.

10-50% polyazophenylene fragments showed the temperatures of 50% weight loss in air to be 35-75°C higher than for polyisoprene (Fig. 5). However, the destruction of these polymers begins at lower temperatures than that of polyisoprene. This can be explained by the presence of weak bonds between azo groups and isoprene units in the macromolecules of copolymers; on heating these bonds break first, causing the evolution of nitrogen.

By means of chromatographic analysis we determined the quantity of nitrogen evolved from the copolymers in vacuo at 300°C. (It is known [8] that azo groups of polyazophenylene, like those of azobenzene, are stable under these conditions.)

The comparison of nitrogen content in the copolymers before destruction with the quantity of gaseous nitrogen evolved during destruction showed that about 20% of the azo groups are at the ends of the polyazophenylene fragments and form weak bonds with the isoprene units.

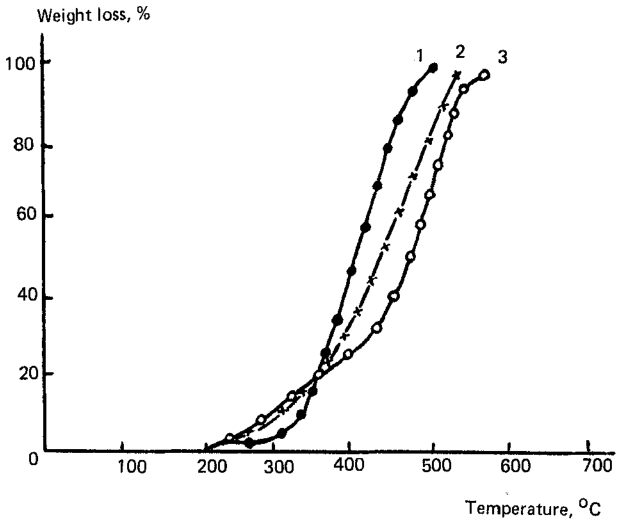


FIG. 5. Dynamic thermogravimetric analysis in air of (1) PI; (2) BI-11; (3) BI-56. Heating rate, 200°C/hr.

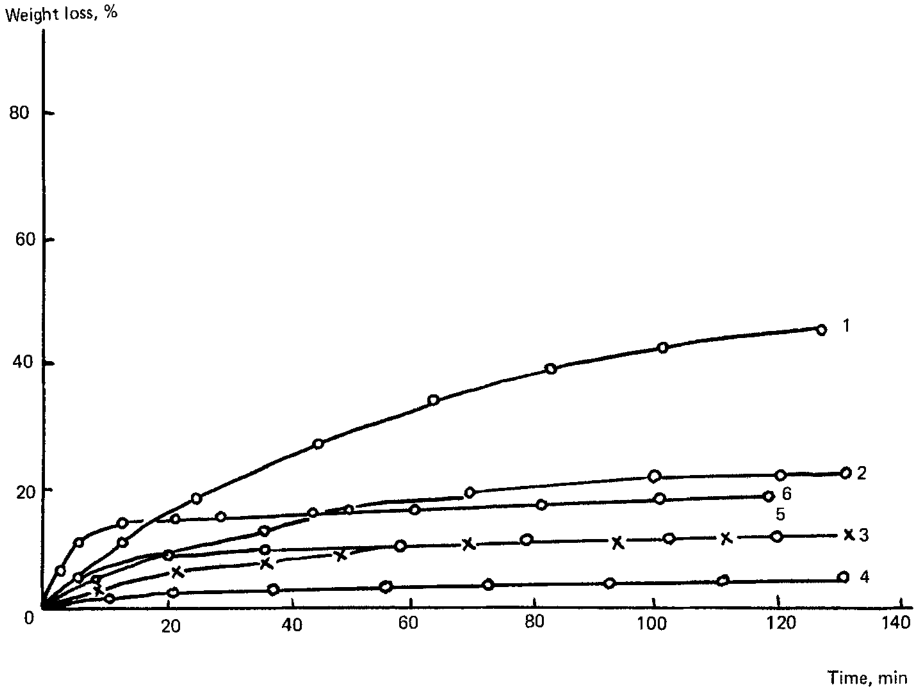


FIG. 6. Isothermal thermogravimetric analysis in air of (1) PI; (2) MI-3; (3) MI-5; (4) MI-16; (5) BI-13; (6) BI-19. Temperature 300°C.

We have undertaken a kinetic study of the destruction of copolymers at 300-450° C in the air and argon and found the temperature coefficients of destruction from the dependence of the initial rate of weight loss on temperature. It was found that the temperature coefficients of destruction in air and argon, respectively, are equal to 74 and 90 kJ/mole for the copolymers while in the case of polyisoprene these values are 90 and 165 kJ/mole, respectively.

The sharp decrease of temperature coefficients for copolymers in argon as compared with polyisoprene indicates that the initiation of copolymer destruction occurs via cleavage of weak bonds between azo groups and isoprene units.

The comparison of the rates of destruction of BI, EI, and SI copolymers with different contents of polyazophenylene fragments shows that the initial rates of weight losses at 300° C are lower for the copolymers containing a smaller amount of polyazophenylene fragments. This is apparently related to the lower content of weak bonds initiating destruction. On the contrary, in the case of MI copolymers, the rate of weight loss decreases with the increase of polyazophenylene fragments content (Fig. 6). This last phenomenon can be explained on the basis of supplemental crosslinking of MI macromolecules through methylene bridge groups between benzene rings.

From the data obtained it follows that the presence of the weak bonds $-CH_2-N=N-$ in the copolymers is the factor determining the elevated initiation rate of decomposition of the copolymers.

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