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Synthesis and Properties of Copolymers Having Polyconjugated Blocks in Macromolecules.

I. Use of Diazonium Salts in Synthesis of Polyazophenylene and Its Copolymers

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ABSTRACT

Polyazophenylene (PAF) with a system of conjugated double bonds was synthesized from benzidinetetrazonium chloride (BTC). PAF gave an EPR signal and showed anomalous viscosity behavior on dilution of its solutions. Copolymers of PAF and isoprene were synthesized by emulsion polymerization by the Gomberg reaction from BTC and isoprene. The copolymers show high thermal and oxidative stability.

A large number of studies have been devoted to the synthesis and investigation of polymers with a system of conjugated bonds. Polyconjugated compounds (PCC) attract increasing attention due to their high thermal and thermooxidative stability, specific magnetic, optical, and electric properties [1]. One of the peculiar features of PCC is strong intermolecular interaction and formation of donor-acceptor complexes of polyconjugated molecules [2]. PCC were shown to possess high radical reactivity and inhibiting activity in the processes of thermal, thermooxidative and photooxidative degradation of polymers [3]. Modification of polymers by means of PCC additives leads to the improvement of structure and physical-mechanical properties of polymer materials [4].

Mechanical mixing of PCC with high polymers is a sometimes ineffective method of modification and stabilization, however, because the incompatibility of PCC with many polymers, poor solubility, and the high tendency of PCC to aggregate make it difficult to disperse them uniformly in polymeric materials.

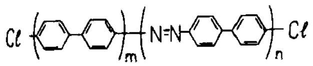
For this reason, we endeavored to find methods which allow synthesis of block copolymers consisting of polyconjugated fragments and blocks of various monomers. Solubility and compatibility of such copolymers can be regulated by the composition of nonconjugated blocks. On the other hand, on the basis of such copolymers new polymer materials can be created.

We consider the introduction of polyconjugated blocks in the macromolecules of elastomers to be of particular interest. In such copolymers, polyconjugated blocks can function as stabilizers against thermal, oxidative and UV degradation. If they contain appropriate amounts of polyconjugated blocks, these copolymers must have the properties of elastoplastics, since the high energies of interaction of polyconjugated blocks and the incompatibility of polyconjugated with elastomeric blocks must yield physical networks like in thermoplastic rubbers of the A-B-A type, where A and B are polystyrene and polydiene blocks, respectively [5].

The synthesis of copolymers having polyconjugated fragments can be performed by radical copolymerization of diene or vinyl monomers with free-radical products of decomposition of aromatic bisdiazo compounds. Under certain conditions, diazonium salts are known to decompose with the formation of aromatic free radicals [6]. The main difficulty is to create conditions which favor two simultaneous processes: polyrecombination of aromatic free radicals with the formation of conjugated fragments and free-radical chain polymerization of vinyl or diene monomer initiated by the end radical of growing polyconjugated block.

The possibility of obtaining polymers with a conjugated system via polyrecombination of radical products from decomposition of aromatic bisdiazo compounds decomposition was shown earlier by Berlin and Parini [7], where the synthesis of polyazophenylene (PAF) from the bisdiazonium salt of benzidine was described.

For the introduction of polyazophenylene blocks into the macromolecules of polymers we studied the transformation of bisdiazo compounds under conditions close to those of the Sandmeyer [8],



PAF

Gattermann [9], and Gomberg [10] reactions. All these reactions have been used previously for the syntheses of PAF. We found that all the above-mentioned reactions of benzidinetetrazonium chloride (BTC) lead to the formation of PAF.

The synthesized polyazophenylenes are brown powders which do not dissolve completely in the usual organic solvents. The yields of PAF were 60-80%; the nitrogen contents of the polymers were in the range 4.5-7.3% (Table 1). The benzene-soluble portion did not exceed 49%, but solubility in sulfuric acid reached 90%. Thus, the cause of poor solubility in organic solvents is more likely to be strong intermolecular interactions of polyconjugated molecules than a network structure of PAF. All synthesized PAF gave a narrow electron paramagnetic resonance (EPR) signal corresponding to a content of paramagnetic centers of about 10^{18} spins/g. PAF did not melt when heated up to 350°C.

The IR spectra of PAF show bands characteristic of aromatic benzene rings at 1600 and 1500 cm^{-1} (stretching vibrations of aromatic C–C bond), an intense band at 820 cm^{-1} (nonplanar deformation vibrations of two adjacent hydrogen atoms in p-substituted benzene rings), and a band of low intensity of 1040 cm^{-1} which can be

TABLE 1. Properties of Polyazophenylenes (PAF) Synthesized from Bisdiazo Derivatives of Benzidine

Type of reaction	Yield (%)	N (%)	Content of paramagnetic centers $\times 10^{-18}$ (spin/g)	Benzene-soluble fraction		Solubility in H_2SO_4 %
				Content, %	$\overline{M}_n$	
Sandmeyer	77	7.3	1.56	43	600	90
Gomberg	70	6.5	1.64	32	750	35
Gattermann	62	4.55	0.83	49	435	54
Hey[a]	40-67	6.5	1.0	3-16	800-1200	40

[a] PAF synthesized from N,N'-bis(nitrosoacetyl)benzidine [14].

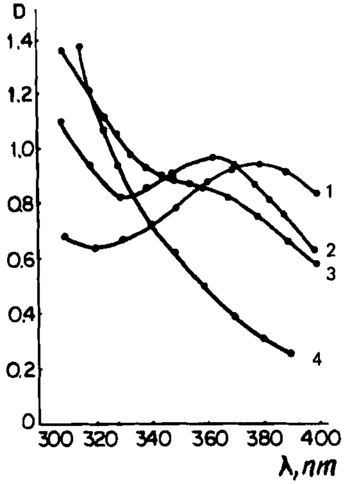


FIG. 1. Electron absorption spectra of polyazophenylenes synthesized via (1) Hey, (2) Gattermann, (3) Gomberg, and (4) Sandmeyer reactions. In benzene, 0.04 g/liter.

assigned to deformation vibrations of the diazo group [11]. Soluble fractions of PAF showed intense bands of monosubstituted benzene ring at 695 and 750 cm^{-1}; this can be explained by the lower molecular weight of soluble fractions and, therefore, the higher content of terminal benzene rings. The number-average molecular weights of soluble fractions were 400-800. Benzene fractions of PAF obtained by different methods had different absorption spectra with maxima in the region 330-360 nm (Fig. 1).

Intermolecular interaction and association of PAF molecules cause an anomalous character of their viscosity curves (Fig. 2). The maximum on the curve is explained by partial dissociation of aggregates on dilution of solutions of PAF.

We carried out numerous experiments but failed to obtain copolymers consisting of PAF and polyisoprene fragments by means of copolymerization of isoprene with products of decomposition of benzidinetetrazonium chloride (BTC) in the presence of cuprous ions or metallic copper (Sandmeyer and Gattermann reactions). Only initiation of isoprene homopolymerization was observed.

The Gomberg reaction was used for the emulsion copolymerization of isoprene and BTC at temperatures of 0°C (polymer GI-1) and 15°C

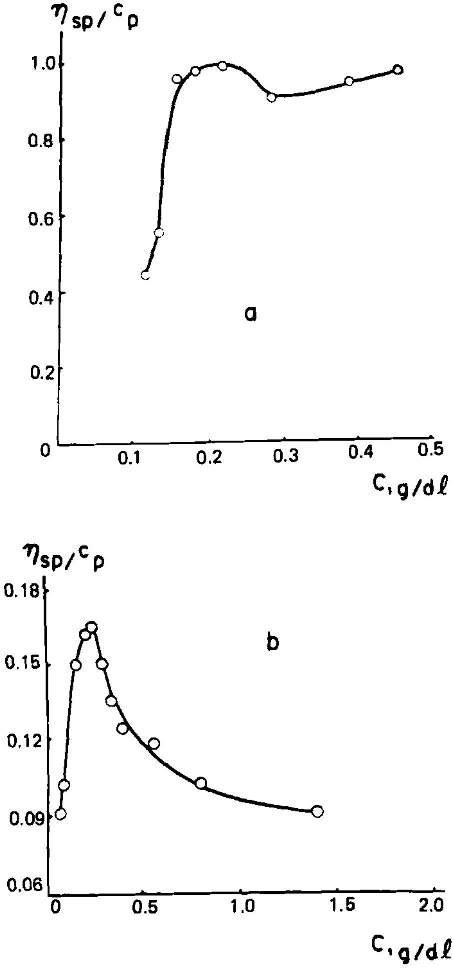


FIG. 2. Dependence of reduced viscosity on concentration of H_2SO_4 solution of polyazophenylene synthesized (a) via Gomberg reaction and (b) via Hey reaction. Temperature 20°C.

(polymer GI-2). The BTC concentration was to 10 wt % relative to isoprene. The polymers synthesized were brown powders which did not dissolve completely in organic solvents. The polymer yield based on BTC was always greater than 100%. The elevation of polymerization temperature leads to an increase in the content of the

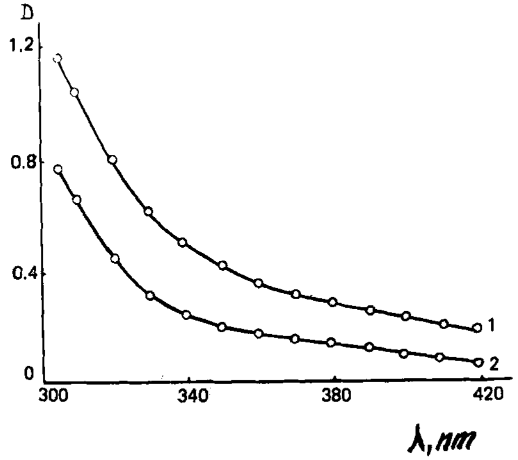


FIG. 3. Electron absorption spectra of (1) copolymer GI-1 and (2) copolymer GI-2. In benzene, 0.04 g/liter.

benzene-soluble fraction from 20.3% (GI-1) to 31.3% (GI-2). The number-average molecular weights of the soluble fractions were 600-800. Soluble fractions softened at 260-320°C and had a wide absorption band in the UV part of the spectrum. The absence of a shoulder on the absorption curves of GI copolymers indicated that copolymers do not contain considerable amounts of PAF homopolymer, which demonstrates a shoulder in the region of 350 nm (Figs. 1 and 3). Nonsoluble fractions did not melt up to 350°C. The copolymers contained appreciable amounts of nitrogen (7-14%).

IR spectra of both soluble and nonsoluble fractions of GI copolymers had bands characteristic of aromatic rings and diazo groups of PAF and absorption bands of polyisoprene in the regions 2850-2950, 1460, 1365 cm^{-1} which were absent in PAF spectra. The copolymers gave a narrow EPR signal with an intensity of 10^{17} spins/g; this is evidence for the presence of conjugated blocks in the molecules.

Viscosity curves obtained on diluting copolymers solutions in H_2SO_4 demonstrate an anomalous character, with a maximum at the concentrations of 0.3-0.5 g/dl (Fig. 4). On the basis of data of elemental analysis and UV, EPR, and IR spectra, a structure for the synthesized GI copolymers can be written. Composition of the copolymers was evaluated from the data of elemental analysis. The

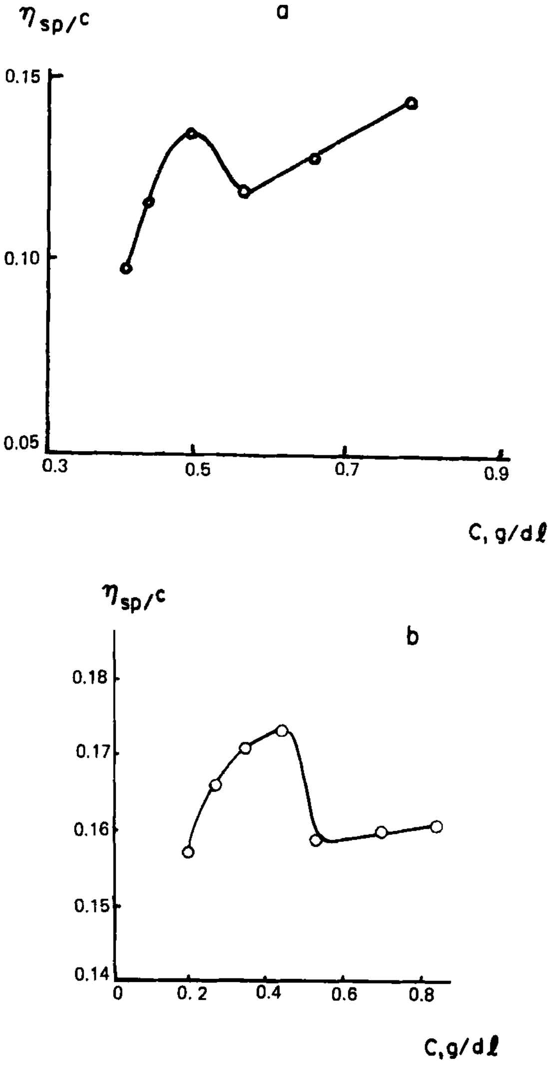
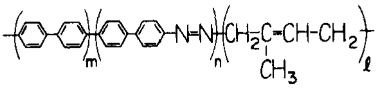
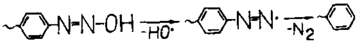


FIG. 4. Dependence of reduced viscosity on concentration of H_2SO_4 solution of (a) copolymer GI-1 and (b) copolymer GI-2. Temperature 20°C.



GI Copolymers

values of the H/C ratio found for copolymers GI-1 (0.0736) and GI-2 (0.0826) correspond to isoprene unit contents of 22.8 and 34.4 wt %, respectively. The higher content of PAF fragments in copolymer GI-1 is consistent with the higher absorption of its solution in the UV region and the higher content of paramagnetic centers (8.4×10^{17} spins/g as compared with 5.4×10^{17} spins/g for copolymer GI-2). The copolymers had considerable contents of nitrogen (up to 14%) which decreased to about half when the polymerization temperature was raised from 0 to 15°C. The elevated nitrogen content in GI copolymers as compared with PAF (6.5%) points out that isoprene polymerization can be initiated by azophenylene radicals formed by stepwise decomposition of diazo compound [Eq. (1)].



(1)

GI copolymers demonstrate an elevated thermal and oxidative stability. At 200°C, polyisoprene oxidizes at a high rate, while the copolymers absorb oxygen at much lower rates, particularly non-soluble fractions (Fig. 5). In argon at 300°C polyisoprene loses about 65% of its weight; weight losses of copolymers under these conditions are 15-16%. When heated in argon atomosphere at 400°C polyisoprene decomposes completely, while weight losses of copolymers GI-1 and GI-2 are 25 and 42%, respectively.

Thus, the use of the Gomberg reaction allows us to synthesize copolymers with a high content of PAF fragments. Copolymers having small and high content of PAF fragments have been synthesized when aromatic N,N'-bis(nitrosoacetyl)diamines were used as a source of aromatic biradicals [12, 13]. The synthesis and properties of such copolymers will be described in a subsequent paper [14].

EXPERIMENTAL

Benzidinetetrazonium chloride (BTC) was obtained by the usual method from $NaNO_2$ and benzidine. PAF and copolymer syntheses were carried out in an argon atmosphere. PAF preparation under

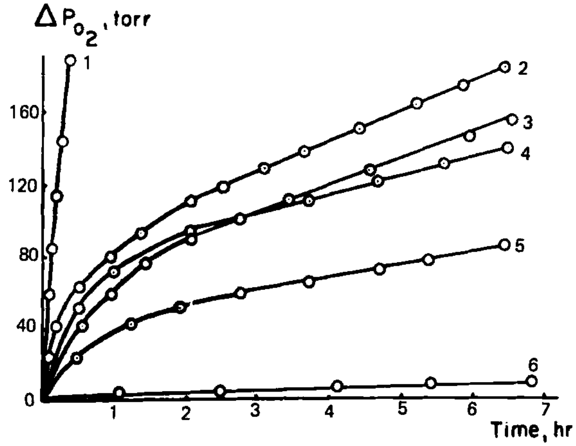


FIG. 5. Kinetics of oxygen absorption by polymers: (1) polyisoprene; (2) soluble fraction of copolymer GI-2; (3) nonsoluble fraction of copolymer GI-2; (4) soluble fraction of polymer GI-1; (5) nonsoluble fraction of copolymer GI-1; (6) polyazophenylene. Initial oxygen pressure 760 Torr; temperature 200°C.

conditions close to those of the Sandmeyer reaction has been described previously [7]. BTC solution was added to the $Cu(NH_3)_2Cl$ solution; PAF yield 77.3%.

The Gattermann reaction was carried out at 0°C. BTC solution was added on vigorous mixing to a suspension of fresh copper powder prepared from zinc powder and $CuSO_4$ solution. The suspension was mixed for 1 hr, then heated to boiling and cooled to room temperature. Copper powder was dissolved on adding diluted HNO_3, and the precipitate was filtered, washed with Na_2CO_3 solution and water to neutral reaction, and dried at 60-80°C to constant weight; PAF yield 61.8%.

To obtain PAF by the Gomberg reaction, BTC solution was added on mixing in an argon atmosphere to an emulsion of benzene in water at 0°C (phase ratio 1:2; emulsifier RSO_3Na, 5% in water). The pH was raised to 7-8 by stepwise addition of NaOH solution, and the emulsion was allowed to heat to room temperature. Mixing was continued for 6 hr; then the mixture was heated to boiling and cooled, and a large excess of methanol was added. The precipitate was filtered, washed with methanol, hot and cold water, and dried at 60-80°C to constant weight; PAF yield 70.0%.

Copolymerization of isoprene with BTC under the conditions of the Gomberg reaction was carried out like the synthesis of PAF (with isoprene instead of benzene as oil phase). Isoprene was twice distilled under argon. After the pH was raised to 7-8 by NaOH solution, the polymerization proceeded for 8 hr either at 0°C or at 15°C. A large excess of methanol was then added; the precipitate was filtered, washed with methanol and water, and dried in vacuo to constant weight.

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