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### Synthesis and Properties of Copolymers Having Polyconjugated Blocks in the Macromolecules. II. The Use of Aromatic N,N'-Bis(nitrosoacetyl)diamines for the Synthesis of Copolymers and Polyazophenylene

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## **Synthesis and Properties of Copolymers Having Polyconjugated Blocks in the Macromolecules. II. The Use of Aromatic N,N'-Bis(nitrosoacetyl)diamines for the Synthesis of Copolymers and Polyazophenylene**

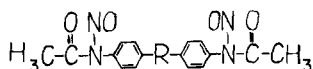
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### **ABSTRACT**

Emulsion polymerization of isoprene and styrene with decomposition products of aromatic N,N'-bis(nitrosoacetyl)diamines leads to the formation of copolymers with different contents of polyconjugated blocks in the macromolecules.

In Part I of this series [1] we described the use of diazonium salts for the synthesis of polyazophenylenes and copolymers containing polyconjugated blocks. Our further investigations [2] showed that more promising compounds for this purpose are aromatic N, N'-bis(nitrosoacetyl)diamines (I);



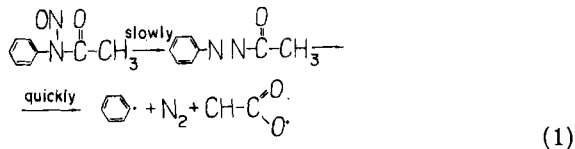
## I

where R is a bridge group:  $-\text{O}-$ (NAE);  $-\text{CH}_2-$ (NAM);  $-\text{SO}_2-$ (NAS); or  $-\text{(NAB)}$ .

To choose the conditions of polyazophenylene and copolymer synthesis providing equal decomposition rates of different diazo compounds we have undertaken kinetic study of decomposition of aromatic N,N'-bis(nitrosoacetyl)diamines.

### KINETICS OF DECOMPOSITION OF AROMATIC N, N' - BIS(NITROSOACETYL)DIAMINES

It is known [3] that aromatic nitrosoacetalamines in solutions isomerize into diazoacetates which decompose quickly with the evolution of nitrogen:



The kinetics of decomposition of nitrosoacetanilide and some substituted nitrosoacetanilides were studied earlier by Hey [4] and Huisgen [5]. We used their method of following the decomposition rate by the volume of gaseous nitrogen evolved.

Figure 1 shows the kinetic curves of evolution of nitrogen for decomposition of N,N'-bis(nitrosoacetyl)-p-phenylenediamine (NAF) in benzene solution. At temperatures below 40°C, nitrogen evolution does not reach a 100% value. This fact can be explained by stepwise decomposition of the nitrosoacetylamine group via formation of azo radicals  $\text{C}_6\text{H}_5-\text{N}=\text{N}\cdot$ . These can recombine with phenyl radicals, and in this way some quantity of the initial nitrogen will be bonded in the reaction products. We have found that at temperatures of 20-35°C a brown powder precipitates from benzene solution of NAF;

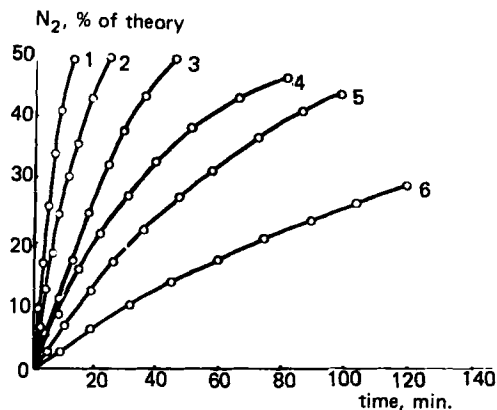


FIG. 1. Evolution of  $N_2$  from  $N,N'$ -bis(nitrosoacetyl)-*p*-phenylenediamine (NAF), 0.0015 mole/liter in benzene: (1) 45°C; (2) 40°C; (3) 35°C; (4) 30°C; (5) 25°C; (6) 20°C.

this product turned out to be polyazophenylene with a nitrogen content of 4-5%. On raising the temperature to 40-45°C the lifetime of azo radicals becomes too short, and the total evolution of nitrogen approaches the theoretical value. The dependences  $\log(X_0/X_t) - t$ , where  $X_0$  and  $X_t$  are initial and current concentrations of NAF, respectively, do not follow a first-order law at the final stages of reaction (Fig. 2). However, these dependences were derived from the curves in Fig. 1 by taking the experimental value of nitrogen evolution to be equal to the degree of NAF decomposition, that is,  $[(X_0 - X_t)/X_0] \times 100\%$ . If the limiting experimental value of nitrogen evolution is accepted to correspond to 100% decomposition of NAF, the dependence  $\log(X_0/X_t) - t$  becomes linear even at the final stages of reaction (Fig. 3). The rate constants calculated from kinetic data give a straight line for the Arrhenius plot (Fig. 4), the activation energy being equal to 80.7 kJ/mole.

The kinetic curves of nitrogen evolution were identical in the case of other  $N,N'$ -bis(nitrosoacetyl)diamines. The results are represented in Table 1.

The values of rate constants and activation energies found in this investigation are close to those obtained by Hey [4] and Huisgen [5] for the isomerization and decomposition of nitrosoacetanilide

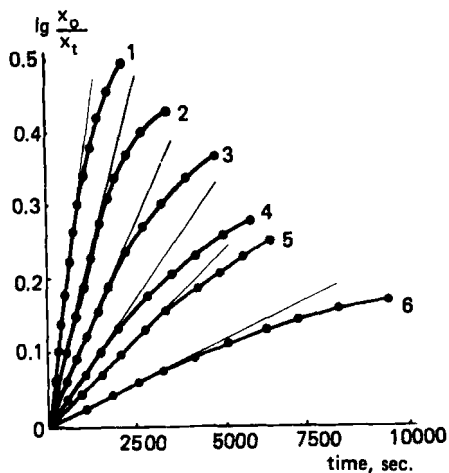


FIG. 2. Kinetics of isomerization and decomposition of *N,N'*-bis-(nitrosoacetyl)-*p*-phenylenediamine (NAF), 0.0015 mole/liter in benzene solution: (1) 45°C; (2) 40°C; (3) 35°C; (4) 30°C; (5) 25°C; (6) 20°C.

( $k_{25^\circ\text{C}} = 1.07\text{--}1.25 \times 10^{-4} \text{ sec}^{-1}$ ;  $E = 90.8\text{--}92.2 \text{ kJ/mole}$ ). The data of Table 1 show that the decomposition rates of different bis(nitrosoacetyl)diamines do not differ considerably, so the synthesis of PAF and copolymers can be carried out under the same conditions.

#### USE OF AROMATIC *N,N'*-BIS(NITROSOACETYL)-DIAMINES FOR SYNTHESIS OF POLYAZOPHENYLENES

Since copolymers of polyazophenylene and polyisoprene have been synthesized by means of emulsion copolymerization of isoprene with decomposition products of bis(nitrosoacetyl)diamines, we studied in detail the model reaction of formation of polyazophenylene from NAB in emulsion system. Syntheses were carried out both in the absence of hydrocarbon phase (PAF-1 and PAF-2) and in the presence of isooctane (PAF-0-1 and PAF-0-2). The phase ratio was 1:2; emulsifier ( $\text{RSO}_3\text{Na}$ ) concentration 5% in water phase; temperature 40°C;

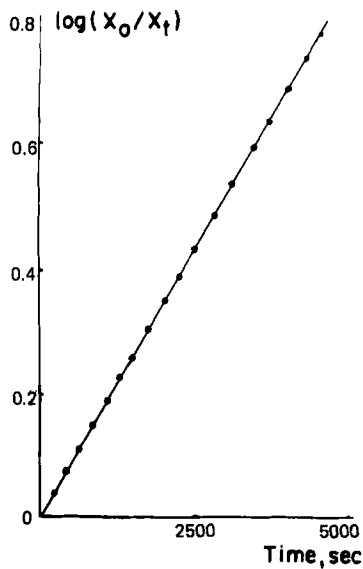


FIG. 3. Kinetics of isomerization and decomposition of NAF in benzene solution. The limiting value of nitrogen evolution is accepted to correspond to 100% decomposition of NAF.

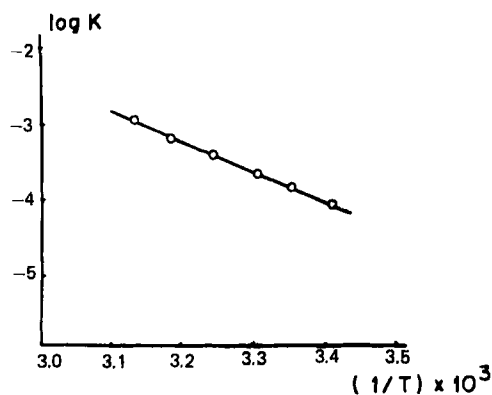


FIG. 4. Arrhenius plot for decomposition of NAF in benzene solution; 30°C.

TABLE 1. Rate Constants and Activation Energies of the Reactions of Nitrosoacetylamine Decomposition in Benzene

	$K \times 10^5$ (sec <sup>-1</sup> )						E (kJ/mole)	$A \times 10^{-10}$
	20°C	25°C	30°C	35°C	40°C	45°C		
DB	9.20	17.8	23.0	49.5	76.0	115.0	80.7	2.4
DF	5.18	10.7	17.3	27.9	46.0	83.3	80.7	1.35
DE	5.35	-	17.3	40.2	55.2	175.0	85.0	7.94
DS	11.80	-	46.0	-	118.0	162.0	84.5	6.32
DM	4.37	15.0	16.9	32.5	46.8	230.0	80.7	8.92

reaction time 10 hr. The amount of NAB was about 1 g/100 ml of water phase in the case of PAF-1 and PAF-0-1 and about 2 g/100 ml in the case of PAF-2 and PAF-0-2. In one of the experiments (PAF-OR-2) tert-dodecylmercaptan (0.4 wt %) was introduced into isooctane; this mercaptan was also used as regulator in copolymerization with isoprene.

Low molecular weight fractions of PAF were removed from the reaction products by Soxhlet extraction with methanol for 10-20 hr. The content of methanol-soluble fraction increased by 50% when regulator was present in the hydrocarbon phase (Table 2).

Both methanol- and benzene-soluble fractions of PAF exhibit a wide absorption band in the UV part of the spectrum with maxima at 350 and 380 nm, respectively (Fig. 5). In IR spectra of synthesized PAF there is a new band at 1720-1740 cm<sup>-1</sup> which was absent in the spectrum of PAF obtained from the tetrazonium salt of benzidine [6]. This band can be ascribed to stretching vibrations of C=O in the acetate group. Apparently, some acetate radicals recombine with phenyl radicals, forming ester groups at the ends of PAF molecules. A low-intensity band at 1720-1740 cm<sup>-1</sup> indicates a small content of acetate end groups.

All the PAF specimens gave a narrow EPR signal corresponding to a content of paramagnetic centers of 10<sup>18</sup> spins/g.

Hence, the decomposition of NAB both in the absence and in the presence of a hydrocarbon phase leads to the formation of PAF via polyrecombination of phenyl and azoradicals. Other aromatic bis(nitrosoacetyl)diamines were also used for the synthesis of PAF having the structure II

TABLE 2. Properties of PAF Synthesized from Bis(nitrosoacetyl)-benzidine

Polymer type	Yield (%)	N <sub>2</sub> evolution, (% of theory)	Content of N (%)	Benzene-soluble fraction	
				Content (%)	$\bar{M}_n$
PAF-17	40.4	43.7	6.4	14.9	1150
PAF-o-17	59.9	37.6	6.1	16.7	870
PAF-34	58.2	39.6	6.5	3.23	1220
PAF-o-34	67.3	33.8	6.8	10.7	800
PAR-OR-34	62.0	37.7	6.7	11.1	1010

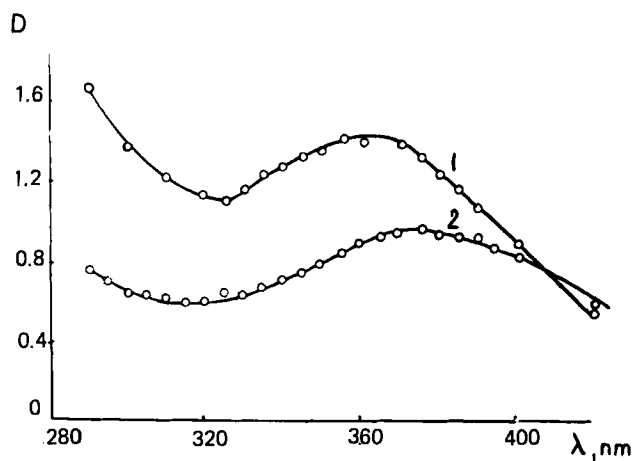
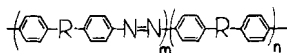


FIG. 5. Electron absorption spectra of (1) methanol-soluble and (2) benzene-soluble fractions of PAF-0-17. Concentration: (1) 0.29/liter; 0.04 g/liter.





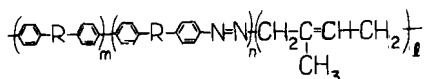
II

where R is  $-(\text{PAF-B})$ ;  $-\text{O}-(\text{PAF-E})$ ;  $-\text{CH}_2-(\text{PAF-M})$ ; or  $-\text{SO}_2-(\text{PAF-S})$ .

The yield, solubility, the content of azo groups, molecular weight of soluble fractions, and the intensity of the EPR signal of the various PAF were rather similar. Only absorption spectra demonstrated some differences caused by introduction of bridges between benzene rings. The benzene-soluble fractions of PAF-B and PAF-S have absorption maxima at 380 and 360 nm, respectively; PAF-M and PAF-E show a broad shoulder in the region of 330-340 nm. A hypsochromic shift in the absorption spectra can be explained by the decrease of effective degree of conjugation in PAF molecules caused by the introduction of bridge groups between benzene rings.

### SYNTHESIS AND PROPERTIES OF COPOLYMERS CONSISTING OF POLYAZOPHENYLENE AND POLYISOPRENE FRAGMENTS

The use of aromatic  $\text{N,N}'$ -bis(nitrosoacetyl)diamines for the emulsion copolymerization with isoprene allowed synthesis of rubber-like polymers (III) consisting of polyisoprene and polyazophenylene blocks [2, 8],



III

where R may be  $-(\text{BI})$ ;  $-\text{O}-(\text{EI})$ ;  $-\text{CH}_2-(\text{MI})$ ; or  $-\text{SO}_2-(\text{SI})$ .

Copolymerizations were carried out in the absence of air at  $40^\circ\text{C}$ ; phase ratio 1:2; emulsifier  $\text{C}_{15}\text{H}_{31}\text{SO}_3\text{Na}$ , 5% in water phase; regulator tert- $\text{C}_{12}\text{H}_{25}\text{SH}$ , 0.4 wt % based on isoprene; reaction time 10 hr. Experimental details are described in a previous work [7].

At initial concentrations of NAB of 1.25-10 wt % (based on isoprene) (0.26-2.1 mole %) the yield of copolymerization products (black-violet elastic polymers) was 9.6-20.7%. To determine the composition of BI copolymers we used the following considerations and experimental observations.

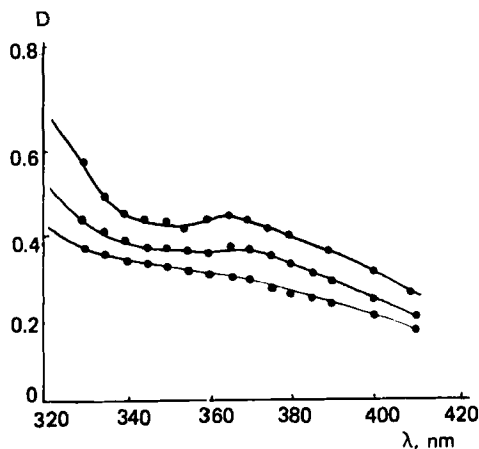


FIG. 6. Electron absorption spectra of copolymer BI (0.1 g/liter) with addition of PAF: (1) 0.005 g/liter; (2) 0.0025 g/liter; (3) 0.001 g/liter.

Firstly, copolymerization products do not contain more than 1-2% PAF homopolymer as impurities because they have no absorption maximum at 380 nm. Figure 6 shows that this maximum appears when purified copolymer BI is mixed with 2.5% PAF. Secondly, the total amount of nitrogen found from the elemental analysis of copolymerization product and from the volume of the gaseous nitrogen evolving in the course of copolymerization was equal to the amount of nitrogen introduced with NAB (in all the experiments the deviations in nitrogen balance were less than 3%). So it can be concluded that the whole quantity of NAB takes part in copolymerization. (This conclusion was borne out later by the elemental analysis data of SI copolymers). Therefore, copolymer composition can be calculated from the copolymer yield and the amount of NAB introduced into the polymerization system. In this way we found that BI copolymers obtained at initial concentrations of NAB of 1.25-10 wt % contain 7-25 wt % PAF fragments (Table 3).

Copolymer solubility drops sharply when PAF fragments content increases; BI copolymers containing more than 20% polyconjugated PAF fragments are practically insoluble in the usual organic solvents.

IR spectra of copolymers BI have both the bands of polyisoprene

TABLE 3. Nitrogen Balance on Isoprene Copolymerization with Decomposition Products of Bis(nitrosoacetyl)benzidine (NAB)

Initial concentration of NAB (wt%) <sup>a</sup>	Polymer yield (%) <sup>a</sup>	N found in polymer		N <sub>2</sub> evolution (% of theory)	Balance of nitrogen (%)
		%	% of N in NAB		
5.0	14.9	2.7	46.8	57	103.8
7.5	18.2	2.9	41.0	57	98.0
10.0	20.7	3.3	39.8	57	96.8

<sup>a</sup>Based on isoprene.

and the bands of benzene rings in the 1600 and 1500  $\text{cm}^{-1}$  region (Fig. 7). The double peak at 1380  $\text{cm}^{-1}$  can be explained by the overlap of bands due to stretching of the C-C bond between benzene rings and deformation of the methyl group; these bands are present in IR spectra of PAF and polyisoprene homopolymers.

According to ESR data, BI copolymers contain paramagnetic centers at concentrations of  $10^{15}$  spins/g; the form of the EPR signal is similar to that of PAF.

All BI copolymers exhibit a broad absorption maximum in the 560 nm region (Fig. 8), whereas in the UV spectrum the absorption maximum at 380 nm, which was present in the spectrum of PAF, (Fig. 6) is absent. The considerable bathochromic shift in electron spectra of BI copolymers as compared with PAF has been explained [8] by the formation of closely packed aggregates PAF blocks. Single PAF fragments in copolymer are apparently not longer and are even shorter than the molecules of PAF synthesized in model conditions. The high flexibility of polyisoprene blocks provides increased mobility of PAF fragments, thus favoring close packing and intermolecular interaction of polyconjugated blocks which are incompatible with polyisoprene blocks. This results in effective formation of donor-acceptor complexes (associates) of PAF fragments and in a sharp increase of effective degree of conjugation, as shown by the position of the corresponding absorption maximum in the electron spectra.

The formation of polyconjugated block aggregates is confirmed by the anomalous behavior of copolymer solutions. Viscosity curves of dilute copolymer solutions show a maximum at concentrations of 0.25-0.35 g/dl (Fig. 9). In the concentration range

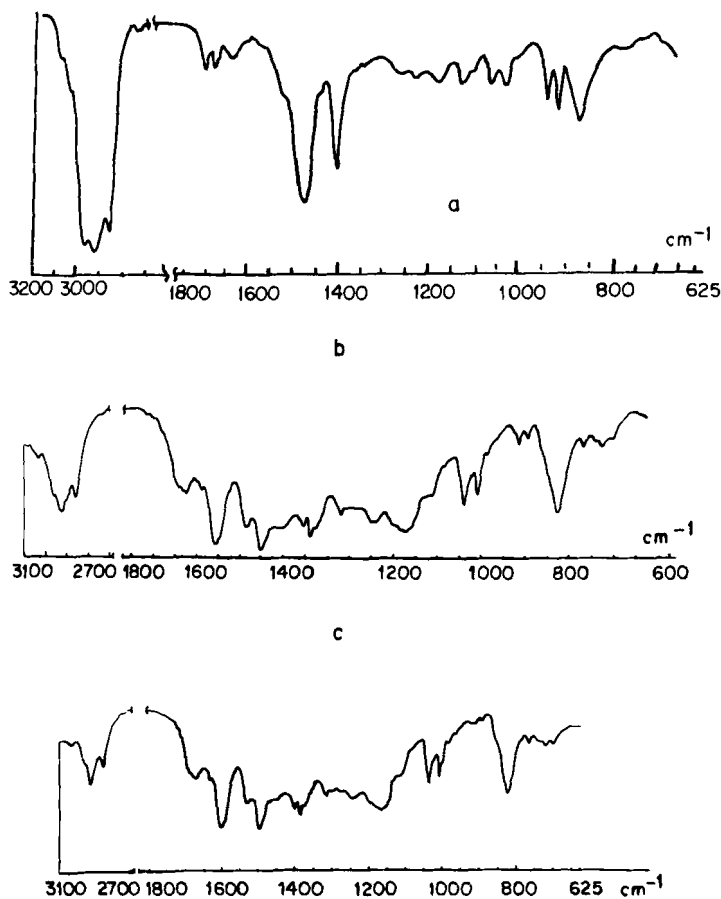


FIG. 7. IR spectra of copolymers: (a) BI-12; (b) BI-56; (c) BI-66.

corresponding to a maximum on the viscosity curves the absorption intensity of copolymers solutions does not follow the Lambert-Beer Law. These anomalies appear to be connected with partial dissociation of the aggregates of polyconjugated blocks.

Apparently, the total degree of  $\pi$ -electron delocalization in the aggregates of PAF fragments substantially depends on the degree of conjugation of separate PAF blocks. An additional increase of resonance energy is conditioned by polarization in the intermolecular  $\pi$ -electron complexes (associates), the latter being determined both by donor-acceptor properties of PAF blocks and steric factors. The

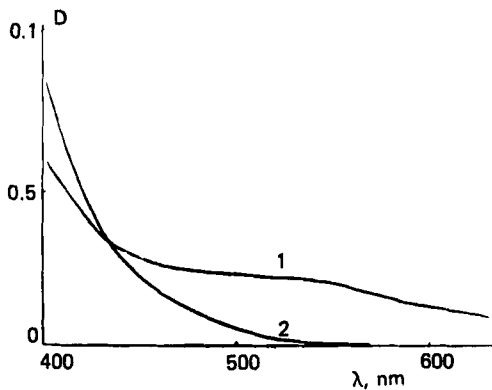


FIG. 8. Electron absorption spectra of benzene-soluble fractions of (1) copolymer BI-56 and (2) copolymer BI-66. Concentration 0.5 g/liter.

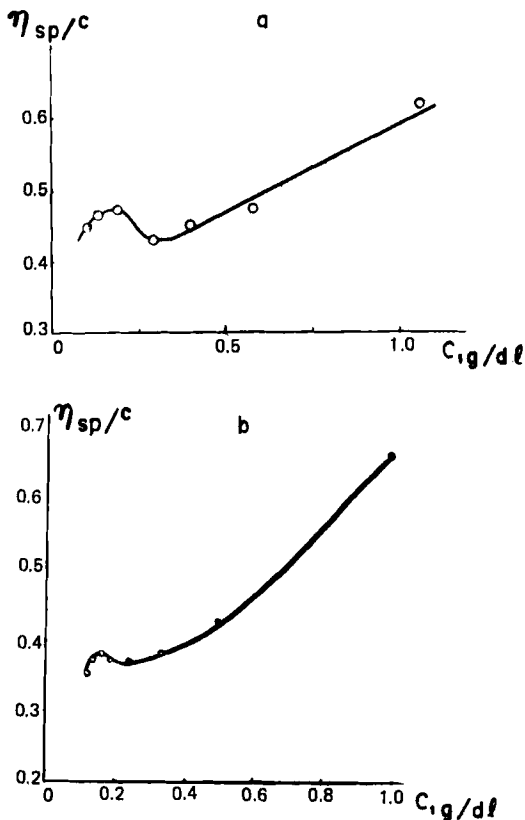


FIG. 9. Dependence of reduced viscosity on concentration of copolymer solution in benzene at 25°C: (a) BI-13; (b) BI-7.

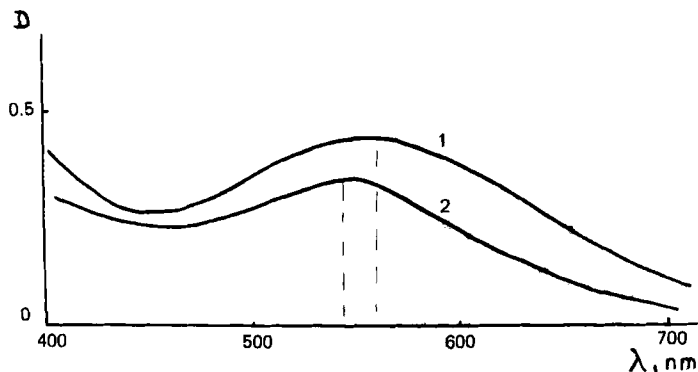
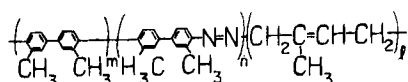


FIG. 10. Electron absorption spectra of (1) copolymer BI-8 and (2) copolymer FI-8 in benzene. Concentration 0.2 g/liter.

length and degree of conjugation of single PAF blocks can be decreased when *N,N'*-bis(nitrosoacetyl)-*p*-phenylenediamine (NAF) is used for the copolymerization with isoprene instead of NAB. Decomposition rates of NAF and NAB are very similar, so under the same conditions of copolymerization PAF fragments of copolymers FI must be shorter than those of copolymers BI.

The comparison of absorption spectra of copolymers FI-8 and BI-8 (figures denote the weight content of PAF fragments) shows that the decrease of PAF blocks length causes a rather small hypsochromic shift of 15 nm (Fig. 10).

To reduce the density of packing of PAF blocks in the aggregates we introduced methyl groups into the benzene rings of PAF fragments. Methyl-substituted oligophenylenes are known to dissolve much better and have lower melting points than corresponding nonsubstituted *p*-oligophenylenes [9]. Using *N,N'*-bis(nitrosoacetyl)-*o*-tolidine for the copolymerization with isoprene we have synthesized copolymer TI having the structure IV



Copolymer TI  
IV

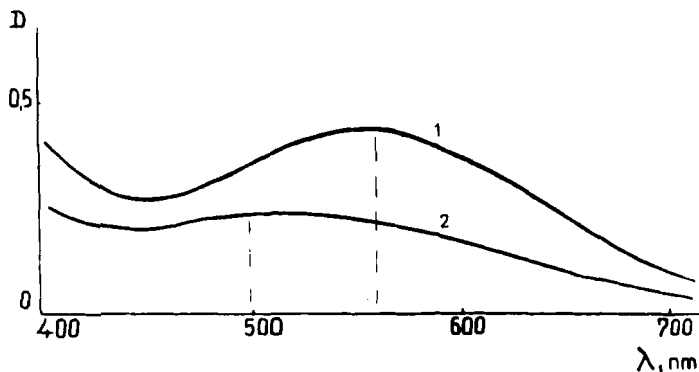


FIG. 11. Electron absorption spectra of (1) copolymer BI-8 and (2) copolymer TI-8 in benzene. Concentration 0.2 g/liter.

In spite of the electron-donating effect of methyl side groups which must raise the degree of conjugation of PAF blocks, the absorption maximum of copolymer TI-8 shifted to 500 nm (Fig. 11). Such a considerable hypsochromic shift is apparently the result of steric hindrance caused by methyl groups which prevent close packing of PAF blocks associates. This conclusion is confirmed by the absence of a sharp maximum on the viscosity curve of copolymer TI as compared with copolymer BI solution. The weakening of intermolecular interaction of polyconjugated blocks having side groups explains the fact that, at equal intrinsic viscosities of 0.35 dl/g, copolymer TI-8 is in viscous flow state and copolymer BI-8 is a highly elastic material.

These results emphasize the importance of intermolecular conjugation and formation of donor-acceptor complexes in polyconjugated systems.

Obviously, the destruction of aggregates of PAF blocks must be accompanied by changes in the optical properties of the copolymers. We discovered that the optical density of the copolymer solution gradually changes on heating both in air and in the absence of oxygen; in the visible region the optical density decreases up to the complete disappearance of the long wavelength maximum, and in the UV region the absorption intensity increases. The process of optical changes is especially pronounced in electron-donating solvents such as tetrahydrofuran. We connected these phenomena with the dissociation of the aggregates of PAF blocks. In the solutions of TI copolymers where intermolecular interaction of polyconjugated blocks is weakened

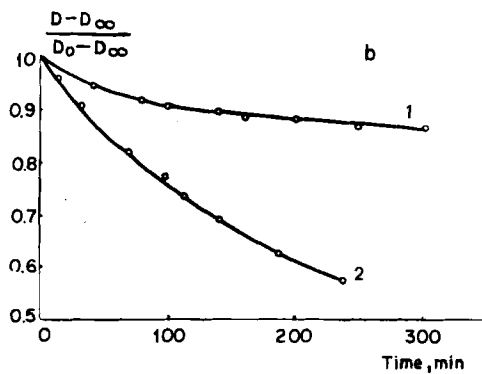
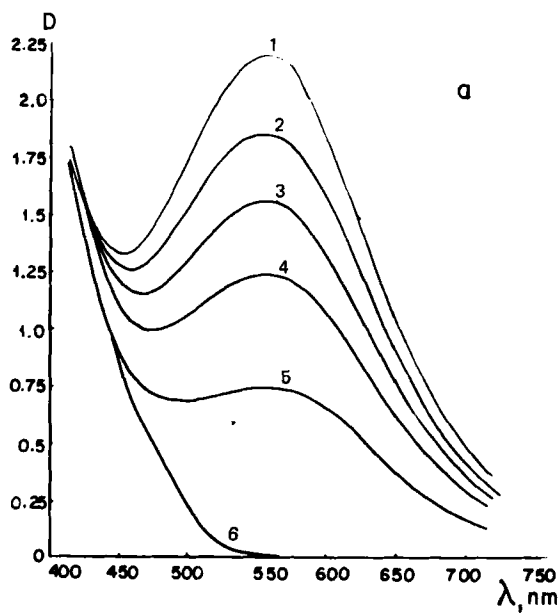


FIG. 12. Spectral changes in tetrahydrofuran solution of copolymer BI-8, concentration 1 g/liter. (a) At 60°C at various times: (1) 0; (2) 50 min; (3) 120 min; (4) 200 min; (5) 550 min; (6) PAF. (b) At (1) 40°C and (2) 60°C as a function of time.



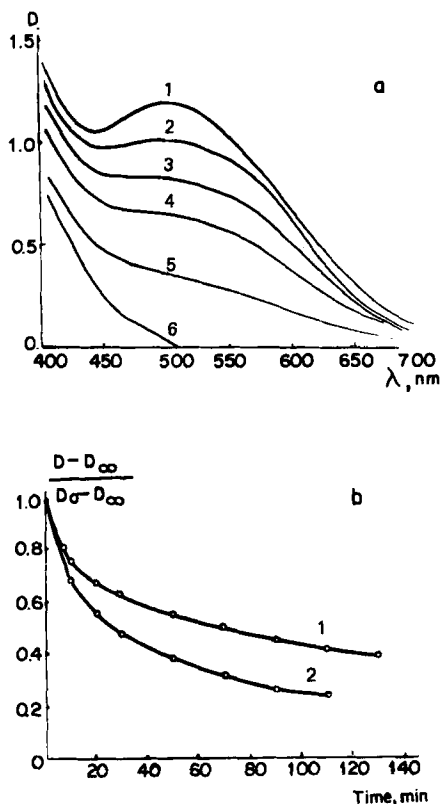


FIG. 13. Spectral changes in tetrahydrofuran solution of copolymer TI-8, concentration 1 g/liter. (a) At 55°C at various times: (1) 0; (2) 50 min; (3) 120 min; (4) 200 min; (5) 550 min; (6) PAF. (b) At (1) 35°C and (2) 55°C as a function of time.

because of steric hindrance of methyl side groups optical changes are faster than in the solutions of copolymers BI.

We have undertaken the kinetic study of this process in the temperature range of 25-60°C. All the experiments were carried out under high vacuum in the absence of oxygen and moisture. Some of the results obtained are shown in Figs. 12 and 13. We have chosen optical densities of copolymer solutions at 660 nm (BI) and 600 nm (TI) as a measure for the evaluation of process rates (Figs. 12b and 13b). The kinetic curves of optical density changes were close

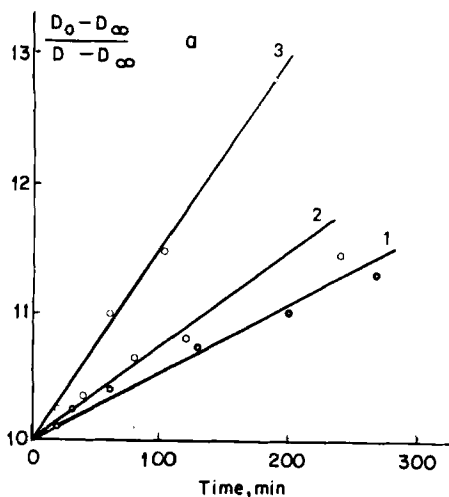


FIG. 14. Determination of effective rate constants for dissociation of polyazophenylene blocks in copolymer BI-8: (1) 40°C;  $K = 0.44 \times 10^{-3}$  liter/mole-min; (2) 50°C;  $K = 0.75 \times 10^{-3}$  liter/mole-min; (3) 60.5°C;  $K = 1.50 \times 10^{-3}$  liter/mole-min.

to straight lines in the coordinates of the second-order reaction (Figs. 14 and 15). The effective rate constants were calculated from the slopes of these curves, and the temperature coefficients of the process were found (Fig. 16). The values of the temperature coefficients were equal to 42 and 50 kJ/mole in the case of copolymers TI and BI, respectively. These data are consistent with stronger intermolecular interaction in BI copolymers as compared with TI copolymers.

Though the change of length of polyconjugated blocks and introduction of side substituents into the benzene rings cause certain changes of optical and other properties of copolymers, the main factor which determines close packing of PAF fragments, effective formation of donor-acceptor complexes, and specific properties of such copolymers is the flexibility of polydiene matrix providing sufficient mobility of polyconjugated blocks.

To change the flexibility of the matrix surrounding polyazophenylene fragments we have synthesized [8] BS copolymers consisting of polystyrene and polyazophenylene fragments (V).

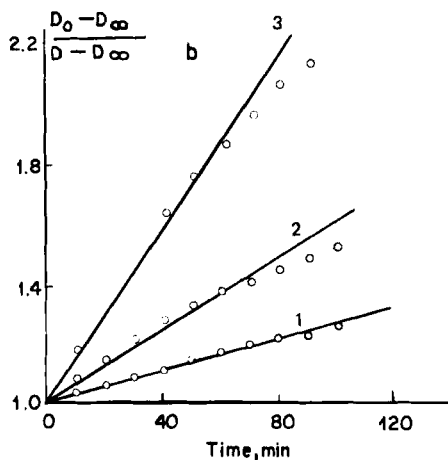
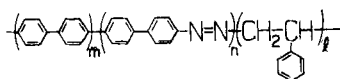


FIG. 15. Determination of effective rate constants for dissociation of polyazophenylene blocks in copolymer TI-8: (1) 25°C,  $K = 2.82 \times 10^{-3}$  liter/mole-min; (2) 35°C,  $K = 6.38 \times 10^{-3}$  liter/mole-min; (3) 55°C,  $K = 14.9 \times 10^{-3}$  liter/mole-min.



### V BS Copolymers

BS copolymers were obtained by emulsion copolymerization of styrene with NAB under the same conditions as BI copolymers. The color of BS copolymers containing 3-10% PAF fragments varied from yellowish-brown to brown; the nitrogen content was about 0.2-0.7%, and the content of paramagnetic centers was about  $10^{16}$  spins/g. BS copolymers dissolve in the usual solvents for polystyrene, giving deeply colored brown solutions which do not demonstrate any anomalous behavior inherent to BI copolymers solutions. In the electron spectra of BS copolymers (Fig. 17) no long wavelength absorption maximum is observed as is in the spectra of BI copolymers. Moreover, the total absorption intensity in the visible region decreases

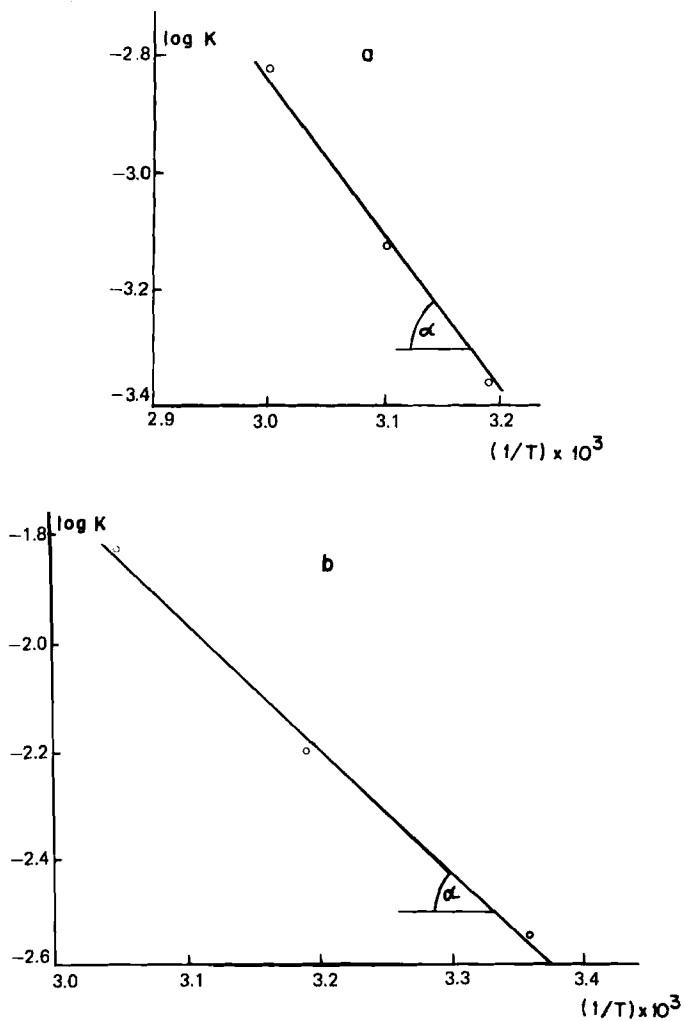


FIG. 16. Determination of effective activation energy for the dissociation of polyazophenylene blocks: (a) in copolymer BI-8,  $E = 50.6$  kJ/mole; (b) copolymer TI-8,  $E = 44.8$  kJ/mole.

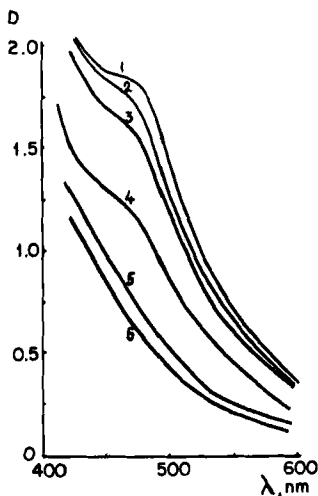


FIG. 17. Electron absorption spectra in benzene of BS copolymers with various contents of polyazophenylene blocks: (1) 11.3%; (2) 8.4%; (3) 5.4%; (4) 3.9%; (5) 3.0%; (6) 2.4%. Concentration 5 g/liter.

sharply compared with copolymer BI, whereas in the UV region there is an increase in absorption caused by the nonassociated form of polyazophenylene blocks.

The great importance of matrix flexibility is confirmed by the change of optical properties of copolymers obtained by the emulsion copolymerization of NAB with isoprene-styrene mixtures. The introduction of increasing amounts of isoprene units into polystyrene matrix drastically changes optical properties: at different isoprene contents the copolymers exhibit absorption maxima at 480, 510, 530, and 560 nm.

These phenomena reflect the cooperative nature of properties of polyconjugated compounds which depend not only on the structure of the single isolated molecules or on  $\pi$ -electron delocalization in separate conjugated chains. The possibility of intermolecular  $\pi$ -electron exchange in polyconjugated blocks associates is an important factor which must be taken into consideration when polyconjugated systems are studied.

EI, SI, and MI copolymers synthesized by the emulsion copolymerization of isoprene with decomposition products of NAE, NAS, and

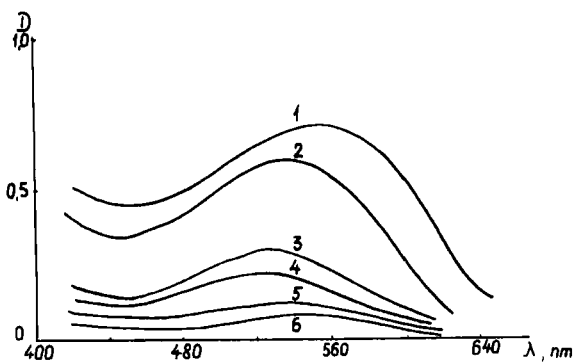


FIG. 18. Electron absorption spectra of copolymers in benzene: (1) BI-8; (2) SI-15; (3) MI-6.5; (4) MI-5.5; (5) EI-3; (6) MI-3. Concentration 0.2 g/liter.

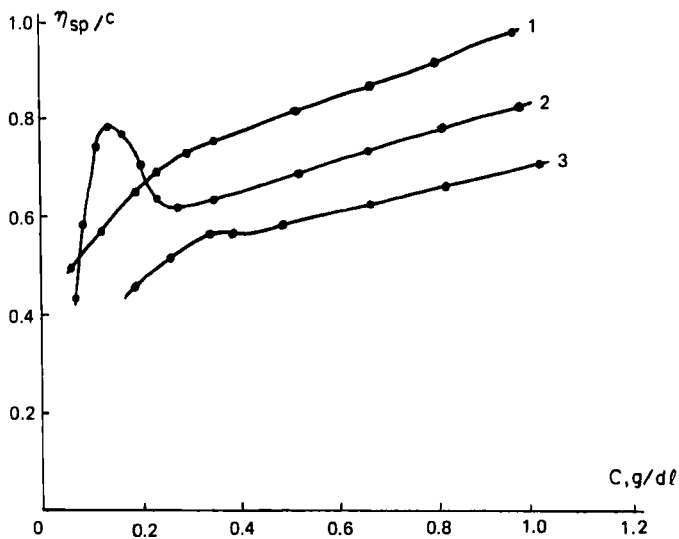


FIG. 19. Dependence of reduced viscosity on concentration of copolymer solution in benzene at 25°C: (1) EI-3; (2) MI-5.5; (3) MI-3.

NAM had properties very similar to those of BI copolymers. Their solutions demonstrated broad maxima in the electron spectra in the 530-540 nm region (Fig. 18). These maxima, as in the case of BI copolymers, are explained by the association of polyazophenylene fragments. The formation of aggregates is confirmed by the anomalous viscosity curves (Fig. 19), maxima on the curves being more pronounced at higher content of PAF fragments in copolymers.

Elemental analysis data of copolymer SI-15 showed that it contains 2.19% sulfur and 0.54% nitrogen. This corresponds to two azo groups for every seven diphenylene sulfone fragments. The same composition has molecules of PAF synthesized from NAS in model conditions. Elemental analysis data of SI copolymers supported the conclusion that the whole amount of nitrosoacetylamine takes part in the copolymerization process.

There are different views in the literature on the role of bridge groups between aromatic rings. Some authors [10-12] consider methylene and other bridge groups to interrupt the conjugation of the chain completely. On the basis of our results we cannot agree with such conclusions. All the synthesized copolymers with bridge groups (MI, SI, EI) contained paramagnetic centers, demonstrated absorption in the visible region, and anomalous behavior in solutions. These are essential properties of polyconjugated systems; complete interruption of conjugation by bridge groups would have changed copolymers properties profoundly as compared with those of BI copolymers, and our results show that this is not the fact.

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