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Abstract

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ON QUASIRADICAL BLOCK COPOLYMERIZATION

(Presented by Academician V. N. Kondrat’ ev on 30 I 1962)

Polymers with a system of conjugated bonds, owing to the considerable difference in the energy spectra of the fractions of polymer homologues, differ sharply in their physicochemical, optical, electrical, and magnetic properties from polymers with saturated chains or isolated multiple bonds ([1], [2]). These systems are characterized by a high tendency to form π-complexes, especially upon interaction of macromolecules that differ from one another in the length of the conjugation chain or that contain double macroradicals in the polymer. The formation of π-complexes should sharply reduce the already comparatively low values of the excitation energies of singlet—triplet or singlet—singlet transitions and, consequently, make such polymers highly reactive. Experimental confirmation of this assumption is provided by the known correlation between the number of conjugated π-electrons, the excitation energies, and the activation energies in reactions of a number of aromatic hydrocarbons with methyl and phenyl radicals ([3]). In accordance with the above, it has recently been shown that polyphenylacetylene and polyazophenylene are capable of block copolymerization with the formation of macromolecular structures possessing a system of π—π conjugation ([1], [2], [4]).

This previously unknown type of polyreaction was proposed to be called quasiradical or radicaloid polymerization ([1]), since in this case chain growth is apparently due to interaction, in the reaction complex, of mesomeric forms of excited macromolecules with active monomers or radicals.

Of especially great interest for the theoretical development and practical application of quasiradical polymerization are polymeric compounds with a system of conjugated benzene nuclei. In this case: 1) the probability of direct interaction of the growing chain with benzenoid structures is excluded, and the picture of the participation in the reaction complex of triplet-excited macromolecules with a system of conjugated bonds becomes clearer; 2) a general method may be created that makes it possible to introduce polyphenylene blocks into various polymers, imparting increased heat resistance and a number of specific properties to the copolymer.

We have carried out experiments on the interaction, in an inert atmosphere at elevated temperature, of benzene-insoluble fractions of polyphenylene (PP) and polyazophenylene (PAP) with paradiztinylbenzene (PDB). In this case PDB was taken in a considerably smaller amount than the indicated polymers. As a result, infusible, insoluble products were obtained in almost quantitative yield.

The elemental composition and certain characteristics of PP and PAP, as well as of the products of their interaction with PDB, are presented in Table 1. The data of elemental analysis indicate the absence of carbonization during the reaction. At the same time, it is seen from Table 1 that the composition of the obtained block copolyme-

Table 1

No.	Polymer type	Block-copolymerization conditions: temperature, °C	Block-copolymerization conditions: duration, h	Yield of insoluble copolymer, %	Found, %: C	Found, %: H	Found, %: N	Found, %: Cl	Calculated, %: C	Calculated, %: H	Calculated, %: N	Calculated, %: Cl	$\overline{M}_n$	Note
1	PF	–	–	–	89.1268.2196.00		–	2.932.82	–	–	–	–	3500	Nonmelting product
2	PF + PDB(2:1 by weight)SP-1	150	6	90	90.5490.3425.56		–	2.012.293085.65			–	1.91		Copolymerization in an argon atmosphere
3	PAF	–	–	–	76.5076.2982.0722.1625.51				16.76	–	–	–	700	Softens in the range 190–200°

Fig. 1. IR spectra

Figure 1: Fig. 1. IR spectra

No.	Polymer type	Block-copolymerization conditions: temperature, °C	Block-copolymerization conditions: duration, h	Yield of insoluble copolymer, %	Found, %: C	Found, %: H	Found, %: N	Found, %: Cl	Calculated, %: C	Calculated, %: H	Calculated, %: N	Calculated, %: Cl	$\overline{M}_n$	Note
4	PAF + PDB(4:1 by weight)SP-2	200	8	95	79.47	[illegible]	[illegible]	[illegible]	[illegible]	4.92	2.18	13.31		Copolymerization in an argon atmosphere

···mers is close to the total composition calculated for the mixture of the starting reagents. In contrast to the initial aromatic polymers, the infrared

Fig. 1. IR spectra: *a* —polyphenylene, *b* —block copolymer of polyphenylene with *p*-diethynylbenzene, *v* —polyazophenylene, *g* —block copolymer of polyazophenylene with *p*-diethynylbenzene.

spectra of the products obtained (see Fig. 1) are characterized by a continuous absorption background over almost the entire spectral region of the sodium chloride prism. Only the absorption bands corresponding to vibrations of benzene rings are distinctly expressed.

It has been shown on extensive experimental material that a continuous absorption background appears in the IR spectra of network structures with a spatial conjugation system (5). Consequently, the products obtained as a result of the interaction of soluble PF and PAF fractions with PDB are block copolymers of network structure with a developed conjugation chain.

The probable mechanism and structure of the copolymer can hardly be expressed by any single structural motif written by means of a valence dash, since in our case the monomer reacts not with functional groups, but with the macromolecular block as a whole. One can only assert that various triplet-excited forms of the macromolecule participate in the reaction complex. For clarity,

Fig. 2. Weight loss versus time at different temperatures.

Figure 2: Fig. 2. Weight loss versus time at different temperatures.

Fig. 3. EPR spectra.

Figure 3: Fig. 3. EPR spectra.

conditionally restricting the number and type of such forms to biradicals with pairing of π-electrons in the terminal phenyl nuclei, the scheme of the reaction of quasiradical polymerization is represented in the following form:

[[displayed chemical reaction scheme: a chlorine-terminated polyphenylene chain $X{-}\mathrm{Ph}{-}[\mathrm{Ph}]_n{-}\mathrm{Ph}{-}X{+}M$ fo

where M is paradivinylbenzene, X is chlorine.

The results of the study of the thermal stability of the starting products and block copolymers are given in Fig. 2. The EPR spectra of the starting PF and PAF, as well as of the block copolymers SP-1 and SP-2 (Fig. 3), are narrow symmetric singlets with a g-factor of 2.00 and distances between the points of maximum slope of 6–9 oersteds. The concentration of unpaired electrons per gram of substance increases for the block copolymers in comparison with the starting products from $5.4 \cdot 10^{18}$ for PAF to $2.0 \cdot 10^{19}$ for SP-2 and from $3.2 \cdot 10^{18}$

Fig. 2. Weight loss with time at different temperatures.
a: 1 —block copolymer SP-2 in an argon atmosphere, 2 —block copolymer SP-2 in air; **b:** 1 —polyphenylene in air, 2 —block copolymer SP-1 in air

Fig. 3. EPR spectra. **a** —polyazophenylene, **b** —block copolymer SP-2, **c** —polyphenylene, **d** —block copolymer SP-1

for PF to $0.9 \cdot 10^{19}$ for SP-1. At the same time, the static magnetic susceptibility of the block copolymers proved to be equal, or close, to zero. This apparent discrepancy can be explained by the fact that in block copolymers, which are products of a network structure, analogously to what occurs in graphite, paramagnetism is masked by diamagnetism ([6]). The temperature dependence of the conductivity of polyphenylenes and block copolymers obeys an exponential law, and the values of the activation energy of conductivity, σ_0 and σ_{300} for the block copolymers are practically no different from the corresponding values for polyphenylenes.

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