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Electrical Conduction Study of Polymers with Indophenine Repeating Units

I. SCHOPOV and C. VODENICHAROV

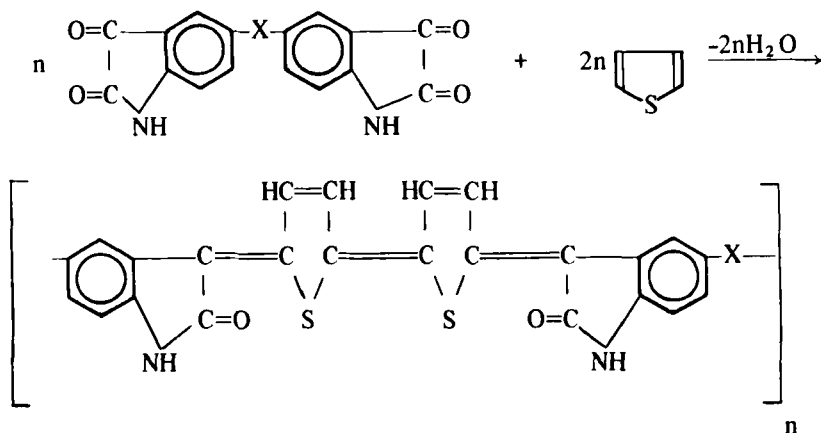
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SUMMARY

It has been established that the dark conduction of isatin-[thiophene]-indophenine and of three polymers in which it is a repeating unit is described by the expression $\sigma = \sigma_0 \exp \{-E_{\text{act}}/kT\}$. The indophenine repeating units in the polymers are connected with a single bond, an oxygen atom, or a methylene group. The electronic spectra in solution and in the solid state indicate that these bonds between the basic units do not interrupt the conjugation along the chain. There is no correlation between the activation energy calculated from optical data and the thermal activation energy of conduction. The latter is considered as a sum of the energy necessary for the generation of the carriers and the energies needed to overcome the intramolecular and intermolecular potential barriers. The values of the parameters characteristic of the semiconducting properties are determined in the first place by the structure of the polymers as a solid body. Crystallinity tends to improve the electrophysical properties. The participation of heteroatoms and groups in the polymer chain, provided they do not interrupt the conjugation, has a favorable effect in cases where their presence improves the intermolecular interaction. A "compensation effect" is to be observed for all substances in vacuum and in air. The experimental data are best explained by the hopping model of electrical conduction.

INTRODUCTION

Not long ago [1-3], through the polycondensation of diisatyls with thiophene, we obtained three polymers that have indophenine as repeating units:



where X is a single bond, an oxygen atom, or a methylene group.

Since the basic unit of these polymers is a vat dye, it is possible to convert it by reduction in a similar manner into a vat (leuco) form. This form is soluble in aqueous alkaline solutions, and this offers an opportunity of utilizing the polymers. By analogy with the vat dyes, it was suggested that these polymers be given the name of vat polymers [1]. This name was adopted by Berlin et al. [4], who synthesized anew the polymer obtained earlier by other authors [5] with indigo as the repeating unit and studied some of its properties. The obtaining of polymers of the indophenine type has been described by other authors as well [6, 7].

It is known that many dyes possess semiconducting properties. Since indophenine polymers have a dye as a repeating unit, it was interesting to study their electrophysical properties and to compare the results with those obtained for the dyes.

EXPERIMENTAL PART

Monomers and Solvents

Thiophene. Reactant puriss. (obtained from the VEB Berlin-Chemie) was redistilled prior to use.

Isatin. Use was made of a commercial product (obtained from the P.P.H. "POCh", Gliwice, Poland) with mp 202-203°.

5,5'-Biisatil. Obtained according to the procedure given by Dethloff and Mix [8] and purified as described earlier [9].

Polyphosphoric Acid (PPA). Use was made of 110% polyphosphoric acid (80% P₂O₅) obtained from orthophosphoric acid (a.p.) and P₂O₅ (a.p.).

Model Compound

Isatin-[thiophene]-indophenine. Isatin (1.47 g, 0.01 moles) was dissolved after continuous stirring in 175 g PPA heated to 40°C. This was followed by adding 0.84 g (0.01 moles) of thiophene. The reaction flask was compactly closed and stirring continued by means of a sealed stirrer for 1 hr at 40°C and for 3 hr at 25°C. The next day the solution was poured into a large volume of distilled water. The dark-blue product which precipitated was filtered off and thoroughly washed with distilled water. After drying, it was found to weigh 1.99 g (93.5%). Its infrared spectrum is very similar to that of indophenine obtained in sulfuric acid according to Steinkopf and Hempel [10].

Polymers

Poly-5,5'-biisatyl-[thiophene]-indophenine. A quantity (2.92 g, 0.01 moles) of 5,5'-biisatyl was dissolved by stirring in 330 g of PPA at 40°C, after which 1.68 g (0.02 moles) of thiophene were added. Stirring was maintained for another 5 hr at 40°C. The next day the dark-blue solution was poured into a large volume of distilled water. The polymer which precipitated was filtered off, thoroughly washed with distilled water, and dried. After continuous extraction with ethanol in a Soxhlet apparatus, followed by drying, a dark-blue powder was obtained which weighed 4.2 g (99%). The inherent viscosity of a 0.1% solution of the polymer in concentrated sulfuric acid is 0.07 dl/g at 20°C.

Analysis calculated for $(C_{24}H_{12}N_2O_2S_2)_n$: C, 67.91%; H, 2.83%; N, 6.60%. Found: C, 63.81%; H, 3.52%; N, 6.50% (after Kjeldahl).

Poly-5,5'-diisatyl ether-[thiophene]-indophenine. Its synthesis has been described earlier [2].

Poly-5,5'-diisatylmethane-[thiophene]-indophenine. Its synthesis has also been described earlier [3].

Electronic Spectra

Electronic spectra were taken on a Leres apparatus in the 400-800 $m\mu$ region in concentrated sulfuric acid at about 0.006 g/liter. The spectra in the visible region in a solid phase were taken in KBr pellets according to the method described in Ref. 11.

Electrical Properties

Pellets 12 mm in diameter and 0.3 to 0.7 mm thick were made from the substances by pressing under 75,000 lb/in.² and in vacuum. Silver electrodes were vacuum deposited on either side of the pellets. The temperature dependence of the electrical conduction was measured in the interval 293-413°K in a measurement cell especially designed to this end. Measurements were taken both upon heating and upon cooling the specimens in air and in vacuum. The aim in the latter case was to obtain a maximum outgassing of the pellets by repeated heating and cooling. The constant vacuum obtained was 10^{-4} torr. The resistance of the pellets was measured by a precise bridge scheme offering a precision of $\pm 0.1\%$ with direct current.

RESULTS AND DISCUSSION

The preparation of the first indophenine polymer was carried out in a medium of concentrated sulfuric acid [1]. It was established later that polyphosphoric acid has a number of advantages [2, 3]. To provide for full comparability of the polymers, poly-5,5'-biisatyl-[thiophene]-indophenine was obtained anew, this time in polyphosphoric acid. The model compound isatin-[thiophene]-indophenine was obtained in the same manner.

Electronic Spectra

The extent of conjugation in the polymers may be evaluated by their electronic spectra. In view of the presence of amide groups in the indophenine molecule, we may expect increased intermolecular interaction resulting from hydrogen bonds. In order to eliminate this influence, the electronic spectra were taken in highly diluted solutions of a rather polar solvent; concentrated sulphuric acid. The electronic spectra in the visible region of the substances are very much alike in shape and of similar intensity. Table 1 shows that, compared with indophenine, a bathochromic shift occurs in the spectra of all polymers. As may be expected, this shift is greatest in the case of poly-5,5'-biisatyl-[thiophene]-indophenine. The bathochromic shift in the other two polymers could not be explained by the inductive effect of the oxygen atom and the methylene group. The spectra of the compounds with similar structure -- 5-methylisatin-[thiophene]-indophenine and 5-methoxyisatin-[thiophene]-indophenine -- show no appreciable inductive effect. The observed bathochromic shift in the spectra of the polymers can be considered as an indication of conjugation along the length of the chains. In the opinion of certain authors [14] the ether linkage interrupts the conjugation, the situation being a problematic one in the case of the methylene group [15]. It was established in the polyindoloquininoxalines and in their model compounds synthesized by us [9, 16], that the ether linkage and methylene group are not an obstacle to conjugation. This was explained by the assumption that what is significant in this case is the fact that the ether linkage and methylene group are located between conjugated sections of considerable length (the indoloquininoxaline repeating units). The conjugated system in indophenine is longer still. In view of the above considerations, it is possible to base the existence of conjugation also upon the participation of oxygen atoms and of methylene groups in the chain in this particular case. As for the manner in which the conjugation is realized, it is possible for it to be p,π -conjugation in the case of the oxygen atom and σ,π -conjugation in the case of the methylene group [17]. Yet another explanation for both cases is that the conjugation may be effected by overlapping the π -orbitals of the aromatic rings whose spatial position may be favorable to this end [18, 19].

Our attempts at taking the visible spectra of the substances in a solid phase, as has been done with certain dyes [20, 21], were unsuccessful. This proved that the absorption wavelengths depend on the thickness of the layer. Reproducible results were obtained upon taking the spectra in

Table 1. Electronic Spectra in the Visible Range of Indophenine and of Polymers with Indophenine Repeating Units

No.	Compound	λ_{\max} , m μ , in H ₂ SO ₄	λ_{\max} , m μ , in KBr	λ_{end} , m μ , in KBr	$\Delta E\lambda_{\max}$, eV	$\Delta E\lambda_{\text{end}}$, eV	ΔE^a , eV
	Isatin-[thiophene]-indophenine	400 660 710	646	708	1.91	1.75	1.48
I	Poly-5,5'-bisatyl-[thiophene]-indophenine	409 673 732	655	715	1.89	1.73	1.36
II	Poly-5,5'-diisatyl ether-[thiophene]-indophenine	401 666 724	683	725	1.81	1.70	1.42
III	Poly-5,5'-diisatylmethane-[thiophene]-indophenine	409 668 726	667	720	1.85	1.72	0.90
IV	5-Methylisatin-[thiophene]-indophenine [12]	398 656 710					
V	5-Methoxyisatin-[thiophene]-indophenine [13]	400 702					

^a $\Delta E = 2E_{\text{act}}$ (E_{act} is determined from electrical measurements).

pellets of KBr. Table 1 shows that, compared with indophenine, the spectra of the polymers display a bathochromic shift. The absorption bands differ from those in solution. This becomes explicable when we take into account the fact that the conformation of the macromolecules in the solid state is determined by the intermolecular interaction as well.

Electrical Properties

The indophenine polymers and the indophenine possess semi-conducting properties. The dark conductivity of all these substances is governed by the well-known expression $\sigma = \sigma_0 \exp \{-E_{\text{act}}/kT\}$. The experimentally determined values from the expression are given in Table 2.

It was established that the values of σ_0 and E_{act} for Polymers I-III, for the earlier polymer [1], and for indophenine are related on one another in the sense of the compensation effect [22-30] (Fig. 1). In accordance with the division made in Refs. 25 and 27, the substances investigated by us must show no compensation effect on account of their low resistance (lower than 10^{13} ohm/cm). It may be maintained that such a fact constitutes rather a confirmation of the view [29] that the phenomenon is of a more general character and that it is manifested upon comparing substances with a similar molecular structure, as in this particular case. The validity of the compensation effect both for the polymers and for the model compound, be it in vacuum or in the presence of oxygen, is probably an indication of an identical electrical conduction mechanism.

The experimental data may, in our opinion, be best interpreted by the hopping model of electrical conduction. There are some objections which may be raised in this case against the barrier tunneling model [31] and the band model [21, 32]. According to these models, the value of E_{act} is determined by the energy necessary for carrier generation. Actually, in many dyes [20, 21] and in a number of low-molecular organic substances [31-33] a correspondence has been established between the activation energy of the dark electrical conduction (calculated from the expression $\sigma = \sigma_0 \exp \{-\Delta E/2kT\}$) and the energy of optical transition determined by the absorption spectrum (in a solid phase). Such a correlation has not been observed in most cases of semiconducting polymers, or the correlations made have been qualitative ones only [22, 23, 34-36]. In our case, according to the method adopted by Vartanian [21], the longest wave bands of the electronic spectra and the end of the absorption (in solid phase) were used in calculating the energies of the singlet-singlet optical transition (Table 1). It is obvious that in all cases these energies are higher than the thermal energies of activation of the electrical conduction. That is why

Table 2. Electrical Properties of Indophenine and of Polymers with Indophenine Repeating Units

Nr	In vacuum			In air		
	E_{act}, eV	$\sigma_{30^{\circ}C}^{-1} cm^{-1}$	$\sigma_0^{-1} cm^{-1}$	E_{act}, eV	$\sigma_{30^{\circ}C}^{-1} cm^{-1}$	$\sigma_0^{-1} cm^{-1}$
	0.74	9.60×10^{-10}	2490	0.65	5.85×10^{-10}	61.1
I						
	0.68	1.38×10^{-10}	60	0.64	3.17×10^{-10}	27.8
II						
	0.71	3.70×10^{-10}	106	0.63	2.58×10^{-10}	6.7
III						
	0.45	1.38×10^{-9}	0.15	0.36	1.26×10^{-8}	0.03

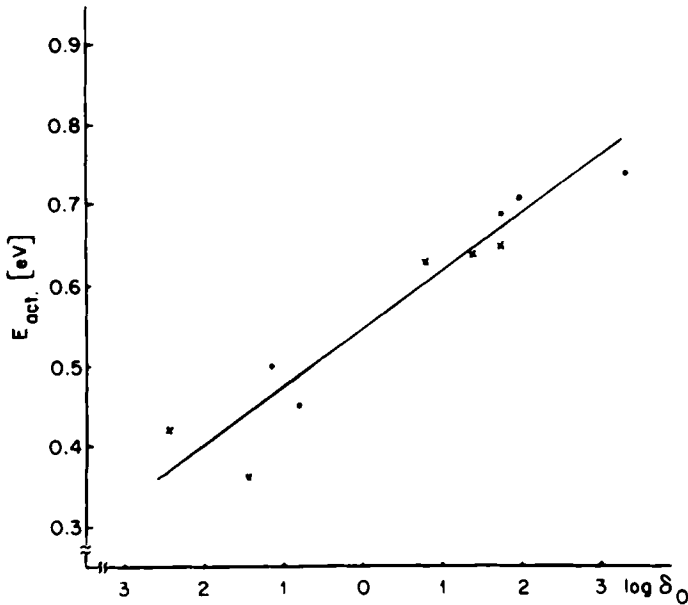


Fig. 1. Compensation effect: (○) in vacuum; (X) in air.

both the band and the barrier tunneling models are inapplicable. The presence of a compensation effect is also an argument against the barrier tunneling model [30]. The hopping model is apparently most suitable. This is often assumed for polymer semiconductors [37-40].

It would be logical to assume that in all cases the charge carriers, generated by one mechanism or another, will move along the length of the indophenine molecule in the same manner. In the polymers, however, upon their passage from one repeating unit into another, they will have to overcome the potential barriers determined by the different spatial position of the indophenine repeating units as well as by the oxygen atom and the methylene group, respectively. Added to this is the energy needed to overcome the intermolecular barriers. On that account the total measured energy of activation of the electrical conduction in the polymers may be conventionally presented by the expression:

$$E_{\text{act}} = E_1 + E_2 + E_3$$

where E_1 is the energy necessary for the generation of the carriers, E_2 is the

energy need to overcome the intramolecular potential barriers, and E_3 is the energy needed to overcome the intermolecular potential barriers.

While the values of E_1 are determined by the extent of conjugation, the factors determining E_2 are quite different. In the indophenine the E_2 term is absent. In the polymers, the problem of the part played by the bridge groups in their chains is related to the value of the energy E_2 . It has been established that the participation of a methylene group in the polymer chain leads in some cases to raising E_{act} and to reducing the electrical conduction [41, 42], while in other cases it leads to opposite results [34, 43, 44]. The improvement of the electrical properties of the polymers in the latter case is explained by the presence of methylene groups which contribute flexibility to the polymer chains, thereby promoting intermolecular interaction and crystallization. This explanation seems applicable to the present instance as well. It does not, however, rule out the realization of conjugation along the length of the polymer chain, since, should the methylene groups "insulate" the individual repeating units, the electro-physical properties of Polymer III and of indophenine are bound to have been very similar, which is not actually the case.

The participation of an oxygen atom in the polymer chain usually leads to raising the E_{act} and to reducing the electrical conduction [14, 41, 45-47], this being explained by interruption of the conjugation by the ether linkage. That this is not the case is shown by the spectroscopic data in the solid phase (Table I) which warrant the conclusion that the conjugation in Polymer II is the highest.

Significant to the examination of E_3 is, in the first place, the structure of the polymer as a solid body, particularly the fact whether it is crystalline or not. The X-ray data obtained showed that only in the case of Polymer III (containing $-\text{CH}_2-$ groups) and of indophenine is it possible to refer to a crystalline structure to some extent. That is why it may be assumed that the low value of E_{act} in the case of Polymer III is determined precisely by this crystalline structure. Such an effect of crystallinity has been established in other polymers as well [43, 44, 48-51]. In the case of indophenine the molecule is shorter than that of the polymers, and the number of the intermolecular transitions is larger. That is why there is a higher E_3 or E_{act} , respectively. * The outstanding role of crystallinity is

*The data published by Kossmehl and Manecke [7] concerning the activation energy and the electrical conduction of indophenine are different from those established by us. This may be due to appreciably differing conditions of measurement. In all probability, however, the explanation lies in the difference in the crystalline structure of the substances, since they have been obtained in different solvents. In much the same manner it is possible to explain also the differences between Polymer I and the one obtained in sulfuric acid [1].

confirmed also by comparison of Polymers II and III. Despite the higher extent of conjugation in amorphous polymer II (with ether linkages in the chains), it displays poorer semiconducting properties compared with the crystalline Polymer III. The ether linkage probably does not contribute sufficient flexibility to the chains, and on that account the intermolecular interaction has been rendered difficult and the polymer is amorphous. Consequently, the higher values of E_{act} observed both here and on other occasions in the presence of ether linkages in polymers are not due to an interruption of the conjugation along the chain by these linkages but are determined by a higher energy of the intermolecular transitions (E_3). That is why any evaluation of the part played by the bridge groups in the polymer chains must always take into account not only the fact whether they are conducive to the realization of conjugation along the chain, but also the influence they may exercise on the structure of the polymer substance. It follows from the experimental data that this structure is very important and that the value of the parameters characterizing the semiconducting properties are determined by them.

The values of E_{act} are lower in a medium of air, as may be seen from Table 2, but their correlations are almost the same as in vacuum.

The electrical conductivities of the substances investigated are in all probability dependent on their structures as well, since the higher values belong to those that are crystalline. In air there is a particularly large increase in the electrical conduction of poly-5,5'-diisatylmethane-[thiophene]-indophenine.

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REFERENCES

- [1] I. Schopov, *J. Polym. Sci., Part B*, **4**, 1023 (1966).
- [2] I. Schopov, *C. R. Acad. Bulg. Sci.*, **21**, 241 (1968).
- [3] I. Schopov, *C. R. Acad. Bulg. Sci.*, **21**, 439 (1968).
- [4] A. A. Berlin, B. I. Liogonkii, and A. N. Zelenetskii, *Vysokomol. Soedin.*, **A10**, 2076 (1968).
- [5] J. Moir, *Proc. Chem. Soc.*, **18**, 194 (1902); DRP 168301, Friedländer, VIII, 437; DRP 3000094, *Chem. Zbl.*, **2**, 937 (1921).

- [6] U.S. Patent 3,334,074; *Chem. Abstr.*, **67**, 82565 (1967).
- [7] G. Kossmehl and G. Manecke, *Makromol. Chem.*, **113**, 182 (1968).
- [8] N. Dethloff and H. Mix, *Chem. Ber.*, **82**, 543 (1949).
- [9] I. Schopov and N. Popov, *J. Polym. Sci., Part A-1*, **7**, 1803 (1969).
- [10] W. Steinkopf and H. Hempel, *Justus Liebigs Ann. Chem.*, **495**, 144 (1932).
- [11] D. T. Longone and H. H. Un, *J. Polym. Sci., Part A*, **3**, 3117 (1965).
- [12] P. Meyer, *Ber.*, **16**, 2269 (1883).
- [13] J. Halberkann, *Ber.*, **54**, 3088 (1921).
- [14] M. I. Gugeshashvili, B. E. Davydov, Ju. V. Korshak, and L. D. Rosenshtein, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **1964**, 1703.
- [15] Ramart-Lucas, *Bull. Soc. Chim. Fr.*, **51**, 289, 965 (1932).
- [16] I. Schopov, *Comm. Dept. Chem., Bulg. Acad. Sci.*, **3**, 47 (1969).
- [17] M. Pestemer and D. Brück, *Methoden der organischen Chemie (Houben-Weyl)*, Band III, T. 2, Thieme, Stuttgart, p. 695.
- [18] G. F. D'Alelio, J. V. Crivello, R. K. Schoenig and T. F. Huemer, *J. Macromol. Sci.-Chem.*, **A1**, 1168 (1967).
- [19] N. Tyutyulkov and D. Petkov, *C. R. Acad. Bulg. Sci.*, **20**, 699 (1967).
- [20] A. T. Vartanian and I. A. Karpovich, *Dokl. Akad. Nauk SSSR*, **111**, 561 (1956); *Zh. Fiz. Khim.*, **37**, 274, 541 (1958).
- [21] A. T. Vartanian and L. D. Rosenshtein, *Dokl. Akad. Nauk SSSR*, **124**, 295 (1959); **131**, 279 (1960); *Izv. Akad. Nauk SSSR, Ser. Fiz.*, **25**, 428 (1961); *Fiz. Tverd. Tela*, **3**, 713 (1961).
- [22] G. N. Demidova, P. N. Pirzkhalava, L. D. Rosenshtein, M. P. Terpugova, and I. L. Kotliarevskii, *Elektrokhimia*, **1**, 1145 (1965).
- [23] B. Krieg and G. Manecke, *Z. Naturforschg., B*, **22**, 132 (1967).
- [24] E. I. Balabanov, A. A. Berlin, V. P. Parini, V. L. Talroze, E. L. Franke-
vich, and M. I. Cherkashin, *Dokl. Akad. Nauk SSSR*, **134**, 1123 (1960).
- [25] V. L. Talroze and L. A. Blyumenfeld, *Dokl. Akad. Nauk, SSSR*, **135**, 1450 (1960).
- [26] A. V. Airapetianz, R. M. Voitenko, B. E. Davydov, and V. S. Serebrianikov, *Vysokomol. Soedin.*, **3**, 1876 (1961).
- [27] V. L. Talroze and L. A. Blyumenfeld, *Vysokomol. Soedin.*, **4**, 1282 (1962).
- [28] F. Beck, *Ber. Bunsenges. Phys. Chem.*, **68**, 558 (1964).
- [29] H. Schmidt and C. Hamann, *Ber. Bunsenges. Phys. Chem.*, **69**, 391 (1965).

- [30] D. D. Eley, *J. Polym. Sci., Part C*, **17**, 73 (1967).
- [31] D. D. Eley and G. D. Parfitt, *Trans. Faraday Soc.*, **51**, 1529 (1959).
- [32] C. Hamann, *Phys. Status Solidi*, **12**, 512 (1965).
- [33] H. Inokuchi and H. Akamatu, *Electrical Conductivity of Organic Semiconductors*, Academic, New York, London, 1961.
- [34] A. A. Dulov, A. A. Slinkin, A. M. Rubinshtein, I. L. Kotliarevskii, M. S. Shvarzberg, V. N. Andrievskii, A. S. Zanina, and S. J. Shergina, *Dokl. Akad. Nauk SSSR*, **169**, 111 (1966).
- [35] L. I. Boguslavskii and L. D. Rosenshtein, *Elektrokhimiya*, **1**, 713 (1965).
- [36] B. Krieg and G. Manecke, *Makromol. Chem.*, **108**, 210 (1967).
- [37] R. M. Voitenko and E. M. Raskina, *Dokl. Akad. Nauk SSSR*, **136**, 1137 (1961).
- [38] A. A. Averkin, A. V. Airapetianz, Yu. V. Ilisavskii, E. L. Lutsenko, and V. S. Serebrianiikov, *Dokl. Akad. Nauk SSSR*, **152**, 1140 (1963).
- [39] A. A. Dulov, *Usp. Khim.*, **35**, 1853 (1966).
- [40] V. S. Mylnikov, *Usp. Khim.*, **37**, 78 (1968).
- [41] B. E. Davydov, Ya. Z. Zakharian, G. P. Karpacheva, B. A. Krentsel, G. A. Lapitskii, and G. V. Khutareva, *Dokl. Akad. Nauk, SSSR*, **160**, 650 (1965).
- [42] A. A. Berlin, B. I. Liogonkii, V. P. Parini, and M. S. Leikina, *Vysokomol. Soedin.*, **4**, 662 (1962).
- [43] A. A. Dulov, A. A. Slinkin, B. I. Liogonkii, and A. M. Rubinshtein, *Dokl. Akad. Nauk SSSR*, **143**, 1355 (1962).
- [44] A. V. Topchiev, Yu. V. Korshak, B. E. Davydov, and B. A. Krentsel, *Dokl. Akad. Nauk SSSR*, **147**, 645 (1962).
- [45] Yu. A. Popov, B. E. Davydov, N. A. Kubasova, B. A. Krentsel, and I. I. Konstantinov, *Vysokomol. Soedin.*, **7**, 835 (1965).
- [46] D. M. Carlton, D. K. McCarthy, and R. H. Genz, *J. Phys. Chem.*, **68**, 2661 (1964).
- [47] D. D. Eley and B. M. Pacini, *Polymer*, **9**, 159 (1968).
- [48] M. Hatano, S. Kambara, and S. Okamoto, *J. Polym. Sci.*, **51**(156), S26 (1961).
- [49] I. L. Kotliarevskii, L. B. Fisher, A. A. Dulov, A. A. Slinkin, and A. M. Rubinshtein, *Vysokomol. Soedin.*, **4**, 174 (1962).
- [50] A. V. Airapetianz, R. M. Voitenko, B. E. Davydov, B. A. Krentsel, and V. S. Serebrianiikov, *Vysokomol. Soedin.*, **6**, 86 (1964).
- [51] L. G. Cherkashina, E. L. Frankevich, I. V. Eremina, E. I. Balabanov, and A. A. Berlin, *Vysokomol. Soedin.*, **7**, 1264 (1965).

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