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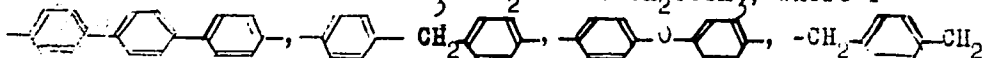
26296
3/190/61/003/008/009/019
B110/B218

AUTHORS: Korshak, V. V., Krongauz, Ye. S., Gribkova, P. N., Basnev,
V. A.

TITLE: Study in the field of coordination-chain polymers. V.
Synthesis of metal-containing polymers of bis- β -diketones

PERIODICAL: Vysokomolekulyarnyye soyedineniya, v. 5, no. 8, 1961,
1203-1209

TEXT: In previous papers (Ref. 1; Vysokomolek. soyed., 1, 1764, 1959;
Ref. 2; ibid. 2, 662, 1960) the authors had shown that coordination-chain
polymers were formed by interaction of bis- β -diketones and acetates (or
acetyl acetonates) of bivalent metals. Bis- β -diketones of the following
structure were studied: $\text{CH}_3\text{COCH}_2\text{CO}-\text{Y}-\text{COCH}_2\text{COCH}_3$, where Y =



Most of these polymers were insoluble and had decomposition temperatures
of between 200 and 400°C. It was the aim of the present work to produce

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polymers with flexible chains, which contained $-(CH_2)_n-$ or $[\text{O}(CH_2)_2]_n$ groups between the benzene nuclei. For this purpose, three aromatic bis- β -diketones were synthesized: 4,4'-bis(acetoacetyl) diphenyl ethane (I); 4,4'-bis(acetoacetyl) ethylene diphenyl ether (II); and 4,4'-bis(acetoacetyl) diphenyl diethylene glycol ether (III). Synthesis was made according to the author's certificate of the USSR, no. 126488, 1959, by acetoacetylating the aromatic compounds by means of acetanhydride in the presence of BF_3 . As compared to Claisen's condensation, the reaction is one-staged and results in a high yield. To prevent formation of intermediates, a large excess of acetanhydride is necessary, molar ratio 1 : 20 - 30. I (melting point 147 - 148°C) was obtained in a yield of 10% referred to diphenyl ethane. The reaction temperature was 40 - 50°C. The infrared spectrum confirmed the structure of p-substituted bis- β -diketone of diphenyl ethane (for keto-enols, characteristic absorption at 1600 cm^{-1} , for 1,4-substituted benzene nuclei, characteristic absorption at 845, and 790 cm^{-1}). As a by-product (10%), diphenyl ethane-
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β -diketone (melting point 81.5 - 82.5°C) was obtained. II (melting point 169 - 170°C) was obtained in optimum yield (16%) at -10°C. The ethylene diphenyl ether, brought into reaction with acetanhydride, was synthesized in the autoclave (150°C, 50 atm) by reaction with sodium phenolate and 1,2-dichloro ethane. III (melting point 125.5 - 126°C, yield 7-9%) was obtained at a reaction temperature of from -5 to +5°C. Diethylene glycol diphenyl ether was synthesized as initial compound by reaction of Na phenolate with β, β' -dichloro diethyl ether (200°C, 50 atm). Since the compounds had not yet been described, the authors synthesized I also by Claisen condensation and found it to be identical with the compound obtained by direct acetoacetylation. Compounds II and III could not be produced according to Claisen. By reacting I, II, and III with acetates of bivalent metals, the authors obtained the compounds given in the Table. In this, they made the following observations: The solubility of the polymer depends on the ionic radius of the metal which forms the polymer chain. It was found that introduction of the groups $-\text{CH}_2\text{CH}_2-$;

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-OCH₂CH₂O-, and -OCH₂CH₂OCH₂CH₂O between the benzene nuclei resulted in coordination-chain polymerization. The molecular weights, determined ebullioscopically, were at about 2000 - 3000. The films produced at 200 - 300°C and 50 atm were brittle. The thermomechanical curves and the X-ray picture of the beryllium compounds of II confirmed the crystal structure of the polymers. There are 3 figures, 1 table, and 6 references: 5 Soviet and 1 non-Soviet.

ASSOCIATION: Institut elementoorganicheskikh soyedineniy AN SSSR
(Institute of Elemental Organic Compounds AS USSR)

SUBMITTED: October 18, 1960

X

Card 4/B/4

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27570
S/190/61/003/009/005/016
B110/B101

AUTHORS: Korshak, V. V., Sosin, S. L., Alekseyeva, V. P.

TITLE: Synthesis of new types of linear polymers

PERIODICAL: Vysokomolekulyarnyye soyedineniya, v. 3, no. 9, 1961,
1332-1340

TEXT: The first two authors showed in previous papers (Ref. 1: Dokl. AN SSSR., 121, 299, 1958; Ref. 2: Vysokomolek. soyed., 1, 938, 1959) that when treating peroxides (PO) of compounds such as p-diisopropyl benzene (DIPB), diisopropyl ferrocene, p-dichloro benzene, etc., linear polymers are formed, and, particularly in the case of DIPB, non-fusible and insoluble polymers with cross-linked trimer structure. Polyrecombination of diphenyl methane (DPM), phenyl acetic acid methyl ester, benzyl benzoate, etc., was studied in the present work. When treating these compounds with tert-butyl peroxide (TBPO) (molar ratio of TBPO to initial compound \gg 1-2) at 200°C, linear polymers were obtained. Diphenyl methane (DPM) gave a linear polymer, an amorphous, yellowish powder which dissolved in benzene (melting point = 200-220°C) with a molecular weight

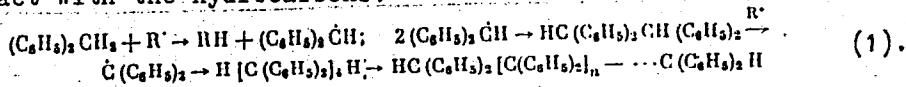
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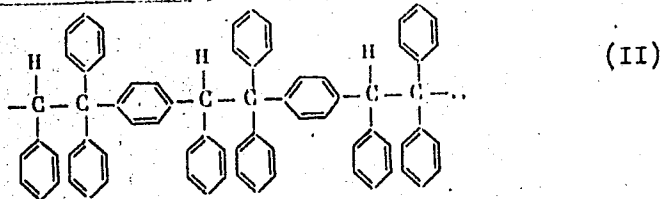
Synthesis of new types ...

(M) of 10,000-900,000, depending on the molar ratio.

$[\eta] = 2.18 \cdot 10^{-3} M^{0.328}$. The following reactions take place:
 $(CH_3)_3COOC(CH_3)_3 \rightarrow 2(CH_3)_3CO \cdot (R \cdot)$; $(CH_3)_3CO \cdot \rightarrow (CH_3)_2CO + CH_3 \cdot (R \cdot)$. The radicals react with the hydrocarbons:



The resultant polydiphenyl methylene (PDPM) (I) does not decompose to free radicals in the presence of diphenyl picryl hydrazine, and is stable to oxidants (HNO₃), since the structure of tetraphenyl ethane (TPE) which is probably formed initially does not permit the formation of stable radicals. Rearrangements might take place according to

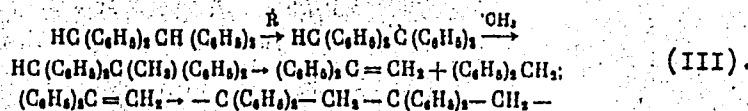


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Synthesis of new types ...

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B110/B101

and



The repeating unit in I and II is: $\text{C}_{13}\text{H}_{10}$, in III: $\text{C}_{14}\text{H}_{12}$. When comparing the IR spectra of the polymers from DPM, TPE, tetraphenyl ethylene, and 1,1-diphenyl ethylene, the absorption maximum characteristic of 1,4-substituted benzene ($833\text{-}840\text{ cm}^{-1}$) was found to be absent in PDPM. Structure II is therefore not possible. III was also excluded since the maximum (760 cm^{-1}) characteristic of the $\text{C}_6\text{H}_5\text{-C-CH}_2$ configuration was absent as well. The PDPM structure according to I is thus confirmed. The dependence of the yield on the molar ratio of PO to hydrocarbon indicated an almost complete consumption of the first peroxide mole for the dimerization (A) of the total DPM to TPE (90% yield). At a ratio of 2 : 1 the polymer yield (B) is constant (50%). This accounts for the

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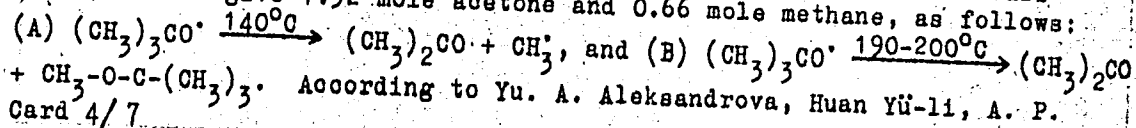
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Synthesis of new types ...

change in viscosity. In A, TPE is formed (melting point 209-211°C, i.e., higher than the reaction temperature), and viscosity considerably increases. In B, however, it decreases since the low-molecular polymers melt already at 180-190°C. The reaction of TPE which is first accelerated is then retarded by the formation of high-molecular polymers (melting point 200°C). The viscosity will be reduced toward the end of the reaction by adding a DPM-PO mixture to DPM; the yield increases. Peroxide admixture of > 2 moles/mole of DPM graphically results in a steep ascent of the molecular weight which asymptotically approaches the ordinate. Assuming that the chain grows by doubling (dimer, tetramer, octamer), the following holds: $N_R = 2 - 2/n$, where N_R = number of free radicals/moles;

n = polymerization coefficient. 1 mole of free radicals is formed on decomposition of TBPO. Maximum M is thus obtained for a PO consumption of 2 moles/mole of hydrocarbon. 0.68 mole tert-butoxyl radicals result from 1 mole PO (in the form of tert-butyl alcohol). 1.32 mole of radicals decomposes to give 1.32 mole acetone and 0.66 mole methane, as follows:

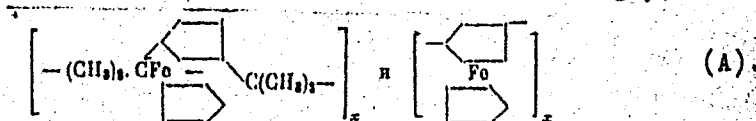


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Pravednikov, S. S. Medvedev (Dokl. AN SSSR, 123, 1029, 1958), no methyl radicals are formed in (B) which takes place at higher temperatures. Isobutylene oxide results on initiation of the peroxide decomposition. The authors separated the fraction (51-53°C): isobutyl-methyl ether and isobutylene oxide. In the same way, they obtained polymers which dissolved in benzene. When using ditolyl methane instead of DPM, a polymer insoluble in benzene and p-cresol (melting point 180-240°C) with cross-linked structure is obtained in addition to linear polymers (melting point = 150-180°C, molecular weight = 2500). The elemental-organic polymers obtained from diisopropyl ferrocene, ferrocene, and triphenyl-tri-N-isopropyl borazol (TPNI) by means of polyrecombination showed IR absorption maxima at 820, 1000, and 1100 cm⁻¹, and, accordingly, structure



M = 1000-7000; they are dark-red powders soluble in benzene (softening point ~300°C). The electron paramagnetic resonance signal (line width, Card 5/7

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120 oe, 20°C) confirmed the existence of unpaired electrons (concentration 10^{21} /g polymer). Treatment of TPNI with TBPO yielded only a soluble, low-molecular polymer. Polyrecombination gives also polymers with aromatic rings in side and principal chains. A soluble copolymer was obtained by treating a mixture of DPM (0.1 mole) and DIPB (0.1 mole) with 0.25 mole TBPO; DIPB alone gave a nearly insoluble polymer. 2,5-dichloro-p-xylene gives a chlorinated analog of poly-p-xylene soluble in benzene. Cl in ortho-position to the CH_3 groups blocks them and prevents their participation in the formation of linear chains. Polyrecombination thus results in carbon chain polymers with aromatic rings in the principal chain, whose production is difficult. Gas chromatography of DPM was made on the X-2 (Kh-2) apparatus. There are 4 figures, 1 table, and 18 references: 6 Soviet and 12 non-Soviet. The three most recent references to English-language publications read as follows: Ref. 7: G. A. Russel, J. Amer. Chem. Soc., 78, 1047, 1956; Ref. 9: J. H. Brook, Trans. Faraday Soc., 53, 327, 1957; Ref. 10: K. M. Johnston, G. H. Williams, Chem. and Chem. Ins. 1958, No. 11, 328.

ASSOCIATION: Institut elementoorganicheskikh soyedineniy AN SSSR
(Institute of Elemental Organic Compounds AS USSR)

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2209, 2409, 1372

27580

S/190/61/003/009/015/016
B124/B101

158000

AUTHORS: Korshak, V. V., Sosin, S. L., Chou Jun-p'ei

TITLE: Production of polymers by thermal dehydropolymerization of hydrocarbons

PERIODICAL: Vysokomolekulyarnyye soyedineniya, v. 3, no. 9, 1961, 1427

TEXT: Heat-treated hydrocarbons are cracked and dehydrogenated, and yield, besides low-molecular decomposition products, resins which are low-molecular condensation products with a complex structure which greatly differs from that of the initial products. Such resins are formed both by gaseous-phase pyrolysis and liquid-phase cracking. High-molecular polymers cannot form under these conditions due to the inevitable decomposition in the high-temperature zone. High polymers may be also obtained, however, when the hydrocarbons are thermally dehydrogenated under conditions preventing thermal degradation of the polymer. The method developed by the authors is based on the liquid-phase dehydropolymerization in a flow of nitrogen on a platinum or tungsten coil electrically heated to 650 - 700°C and immersed in the liquid hydrocarbon. The hydrocarbon

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is dehydrogenated on the coil, and simultaneously forms polymer products which are immediately carried along from the heated surface by the liquid hydrocarbon. The condensation products obtained are led from the high-temperature zone to a heated container where the drops of the condensation products are collected, and the unreacted hydrocarbon is distilled off and recycled to the reactor (see Fig.). A number of alkyl and hydroaromatic hydrocarbons was treated in this way. Tetralin is converted to naphthalene ~~under the conditions~~ described, whereas polymers are recovered from p-xylene, cumene, ethyl benzene, and p-diisopropyl benzene; the molecular weight of the polymers obtained from p-diisopropyl benzene is about 10,000. The yield in polymer is 10 - 15% related to the hydrocarbon used, and 70 - 80% related to the reacted hydrocarbon. There is 1 figure. [Abstracter's note: Essentially complete translation.]

SUBMITTED: January 12, 1961

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28176

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S/190/61/003/010/004/019
B130/B110

AUTHORS: Korshak, V. V., Krongauz, Ye., S., Sheina, V. Ye.

TITLE: Studies in the field of coordination polymers. VI.
Synthesis of coordination polymers of some bis-(β -diketones)

PERIODICAL: Vysokomolekulyarnyye soyedineniya, v. 3, no. 10, 1961,
1456-1461

TEXT: The authors synthesized aliphatic bis-(β -diketones): 1,1,2,2-tetraacetyl ethane (I), adipyl- (II), and sebacyl diacetophenone (III), and prepared and studied their metal polymers. They prepared I from a suspension of 0.5-mole Na-acetyl acetonate in ether by adding a solution of 0.5-mole iodine in ether at room temperature under vigorous stirring.

The melting point was 185-186°C, the yield 27-30%. II and III were prepared according to V. V. Korshak et al. (Vysokomolek. soyed., 1, 1764,

1959). The melting point of III was 108-109.5°C (Yield 20-22%). The metal polymers of the bis-(β -diketones) produced were prepared by 3-hr heating in a vacuum of 2-4 mm Hg of their equimolecular mixture with the

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respective Me-acetyl acetonate at 150-210°C until no acetyl acetone was set free. To remove the remaining acetyl acetone, the resulting product was treated with hot water, boiled in alcohol, washed with ether, and dried to constant weight. The copper derivatives were obtained by reaction of the diketones with copper acetate in an alcohol solution. It was found that I with Be-, Ni-, Co-, and Zn-acetyl acetonates formed nonfusible powders which were insoluble in ordinary organic solvents and had a high decomposition temperature. I formed no coordination compounds with Mn and Cd. The chemical analysis showed that the composition of the resulting metal compounds corresponded to the theoretical values. Also the metallic derivatives of II and III constituted colored powders. The Be-derivatives of III, and the Be-, Zn-, and Cd-derivatives of II, are soluble in chloroform, tetrachloro ethane, dioxane, bromo benzene, and dimethyl formamide, the Ni- and Co-derivatives only in dimethyl formamide and dioxane. The peculiarities of these compounds are explained according to Hammond, Borduin, and Guter (see below). In the interaction between tetraacetyl ethane and the metal ions, a coordination binding of the metal takes place between the keto groups of adjacent molecules of the

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binding agent (Fig. 1). In II, and particularly in III, the formation of closed, monomeric complexes is probable because of the presence of a flexible methylene chain (Fig. 2). There are 2 figures, 3 tables, and 6 references: 2 Soviet and 4 non-Soviet. The four references to English-language publications read as follows: R. G. Charles, Organic Syntheses, 39, 61, 1959; G. S. Hammond, W. G. Borduin, G. A. Guter, J. Amer. Chem. Soc., 81, 4682, 1959; G. A. Guter, G. S. Hammond, J. Amer. Chem. Soc., 81, 4686, 1959; G. J. Bullen, Acta crystallogr., 12, 703, 1959.

ASSOCIATION: Institut elementoorganicheskikh soyedineniy AN SSSR
(Institute of Elemental Organic Compounds AS USSR)

SUBMITTED: October 25, 1960

Fig. 1. Model of a 1,1,2,2-tetraacetylene ethane complex with metal,
• carbon, o --hydrogen, O-- oxygen, ⊙ -- metal.

Fig. 2. Model of a sebacyl diacetophenone complex with metal. Designations
as in Fig. 1.

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28177

S/190/61/003/010/005/019
B130/B110

5.3830

AUTHORS: Korshak, V. V., Mozgova, K. K., Shkolina, M. A.

TITLE: Synthesis of graft copolymers. VII

PERIODICAL: Vysokomolekulyarnyye soyedineniya, v. 3, no. 10, 1961,
1462-1467

TEXT: The authors describe the possibility of producing graft copolymers from polyamide and polyester films and vinyl monomers without the use of ozone. Films of mixed polyamide Γ -669 (G-669) stored for different periods of time were used for the investigation. The monomer used was styrene. Tests showed that a freshly prepared polyamide grafted only 2-3% polystyrene, a one-year old up to 9%, and a 6-year old 30-60%. In the 6-year old polyamide, active centers formed by the action of atmospheric oxygen and moisture. The effect of atmospheric oxygen and air was studied at various temperatures. It was shown that a sample grafting no more than 2.5% polystyrene, grafted 20% after thermal treatment in air at about 80°C. In thermal treatment of caprone films, grafting was also

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Synthesis of graft copolymers. VII

increased but not to such an extent as in the treatment of G-669. Lavsan films heated in nitrogen showed better grafting than those not heated, but did not attain such a degree as when heated in an air flow. The tests also showed that the heating did not only activate the polymers but also improve their mechanical properties. The breaking elongation of Lavsan

films heated at 80°C increased by 48.8%, that of caprone films by 176%. No positive results have been obtained yet when trying to find free radicals by an epr spectrum. Infrared and ultraviolet spectra showed no considerable change due to thermal treatment of caprone. The ultraviolet spectrum of heated Lavsan suggested a formation of groups containing CO. γ -ray patterns showed higher orderliness of the molecular chain of heated samples. The breaking elongation of samples was tested at the VNIIS, the infrared and ultraviolet spectra were taken at I. V. Obreimov's laboratory, the X-ray pictures at A. I. Kitaygorodskiy's laboratory. A. V. Zasechkina and A. I. Volkova assisted in experiments. There are 2 figures, 8 tables, and 6 Soviet references.

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Synthesis of graft copolymers. VII

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ASSOCIATION: Institut elementoorganicheskikh soedineniy AN SSSR
(Institute of Elemental Organic Compounds AS USSR)

SUBMITTED: November 3, 1960

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28180

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S/190/61/003/010/009/019
B124/B110

AUTHORS: Korshak, V. V., Vinogradova, S. V., Morozova, D. T.

TITLE: Study of coordination polymers. VII. Coordination polymers based on quinizarin and 4,4'-bis-(acetoacetyl) diphenyl ether

PERIODICAL: Vysokomolekulyarnyye soyedineniya, v. 3, no. 10, 1961, 1500 - 1508

TEXT: The authors synthesized the homogeneous coordination polymers of quinizarin (I) with Mg, Ca, and Be, the coordination polymers of (I) with two different metals and, finally, the coordination polymers on the basis of (I) and 4,4'-bis-(acetoacetyl)biphenyl ether (II) with Zn, Cu, Mn, Ni, Co, Mg, Ca, Cd, and Be, and studied their properties. The results obtained with homogeneous coordination polymers and mixed coordination copolymers are given in Tables 1 - 4. The studied polymers were homogeneous, solid, powder-like substances of intense color, practically insoluble in chloroform, dichloro ethane, tetrachloro ethane, a mixture of tetrachloro ethane and phenol, chloro benzene, methanol, dimethyl formamide, ditolyl methane, dioxane, tetrahydrofuran, methyl-ethyl ketone, ethyl acetate, and cresol

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Study of coordination...

except for the coordination polymers of beryllium, which were rather easily soluble in chloroform, cresol, and dimethyl formamide. The molecular weights of polymers of I with Be varied from 1700 - 1800 and from 3500 - 3600. As proved thermomechanically mixed coordination polymers of I with Zn and Cd or Zn and Cu are more stable than the respective homopolymers. This is reverse with Be polymers. Heat deformation of all compounds was found between 200 - 450°C (no chemical decomposition). As proved by X-ray tests most of them consist of crystalline and amorphous phases together. The synthesis was carried out by heating the ligands solved in dimethyl formamide in N₂ current at 120°C, addition of the metal compound solved in dimethyl formamide at 100°C, and 1 hr heating at 120°C, 1 hr at 120 - 140°C, 4 hr at 140°C. The authors thank the collaborators of the laboratories of INEOS AN SSSR under supervision of G. L. Slonimskiy, A. I. Kitaygorodskiy, and N. E. Gel'man. Ye. S. Krongauz and V. Ye. Sheina (Ref. 3; Vysokomolek. soyed. 2, 662, 1960) are mentioned. There are 4 figures, 4 tables, and 5 Soviet references. X

ASSOCIATION: Institut elementoorganicheskikh soyedineniy AN SSSR
(Institute of Elemental Organic Compounds AS USSR)

Card 2/3

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29733
S/190/61/003/011/002/016
B124/B101

AUTHORS: Korshak, V. V., Slinkin, A. A., Vinogradova, S. V.,
Babchinitser, T. M.

TITLE: Study in the field of coordination chain polymers.
VIII. Coordination polymers based on bis-(8-hydroxy-
quinolyl)methane, quinizarin, and 4,4'-bis-(aceto-
acetyl)phenyl ether

PERIODICAL: Vysokomolekulyarnyye soyedineniya, v. 3, no. 11, 1961,
1624-1632

TEXT: The synthesis of mixed coordination polymers of bis-(8-hydroxy-
quinolyl)methane (I) and quinizarin (II), (I) and 4,4'-bis-(aceto-
acetyl)phenyl ether (III) with various metals is described, and the
magnetic properties of some coordination polymers of (II), (I), and (III)
are studied. Compositions, structures, and properties of the synthesized
coordination polymers are given. X-ray data indicate that the
homogeneous coordination polymers exhibit a more or less ordered
structure. The solubilities of the homogeneous and the mixed coordination

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polymers in organic solvents are extremely low; only the mixed coordination polymers of (I) and (III) with Cu are soluble in cresol. The temperature dependence of the magnetic susceptibility (χ) as well as the magnetic moment and the Weiss constant calculated from the magnetic susceptibility are given for a number of coordination polymers on the basis of (II), (I), and (III). Conclusions as to the configurations of Co, Mn, and Ni in the polymers were drawn from the magnetic properties. The authors thank the staff of the Laboratories of INOES AN SSSR under the guidance of A. I. Kitaygorodskiy and N. E. Gel'man. There are 3 figures, 3 tables, and 7 references: 6 Soviet-bloc and 1 non-Soviet-bloc. The reference to the English-language publication reads as follows:
D. P. Craig, A. Maccoll, R. S. Nyholm, L. E. Orgel, L. E. Sutton, J. Chem. Soc. 1954, 332, 354.

ASSOCIATION: Institut elementoorganicheskikh soyedineniy AN SSSR
(Institute of Elemental Organic Compounds, AS USSR).
Institut organicheskoy khimii im. N. D. Zelinskogo AN SSSR
(Institute of Organic Chemistry imeni N. D. Zelinskiy, AS USSR)

SUBMITTED: November 16, 1960

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29734

S/190/61/003/011/003/016
B124/B101

AUTHORS: Korshak, V. V., Fedorova, L. S., Kolesnikov, G. S.

TITLE: Synthesis of polyarylenealkyls. XI. Chemical properties of poly(halophenylene)ethyls

PERIODICAL: Vysokomolekulyarnyye soyedineniya, v. 3, no. 11, 1961, 1644-1649

TEXT: The degradation of poly(fluorophenylene)ethyl effected by phenyl fluoride, as well as the aspects of hydrogenation and of substituting a hydroxyl and an amino group, respectively, for the halide atom in poly(halophenylene)ethyl were studied in this paper. The effect of the phenyl fluoride concentration on the degradation of poly(fluorophenylene)ethyl (I) has been investigated using a weight ratio of $AlCl_3$ to (I) equal to 1:4, constant temperature ($100^{\circ}C$) and reaction time (4 hr), while the phenyl-fluoride - I ratio was varied. The molecular weight of the initial (I) was 3810; results are presented in Table 1. Data obtained for a phenyl-fluoride - I weight ratio of 5:1, at constant temperature ($100^{\circ}C$) and reaction time (4 hr), and varied $AlCl_3$ - I ratio

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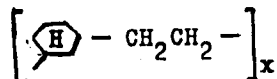
Synthesis of polyarylenealkyls...

are given in Table 2 and, finally, results obtained with a constant phenyl-fluoride - I weight ratio of 5:1, constant $AlCl_3$ concentration of 2.5 per cent by weight of the polymer, constant temperature ($100^\circ C$) and varied reaction time are presented in Table 3. From these results, it can be concluded that phenyl fluoride effects degradation of the polymer, and that the intensity of this degradation is influenced by the ratio of the initial substances, catalyst concentration, and the time of the degradation process. Hence, it follows that phenyl fluoride acts both as a component of chain formation and as a degradation agent in polycondensation with dichloroethane. From the fact that no hydrolysis occurs when poly(chlorophenylene)ethyl is heated to $300^\circ C$ with water in a ratio of 1:10 in the digester, the conclusion may be drawn that the mobility of the chlorine atom in (II) is very low. When (II) is heated with aqueous KOH, hydroxyl groups are substituted for chlorine, and linear molecules formed are cross-linked by oxygen bridges; the properties of the products depend on the amount of reacted KOH. Neither degradation of (II) nor substitution of an amino group for chlorine has been effected by aqueous ammonia solutions. Poly(cyclohexylene)ethyl

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Synthesis of polyarylenealkyls...

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forms when (II) is hydrogenated in benzene in the presence of Raney's nickel catalyst which is not accompanied by degradation. There are 3 tables and 6 Soviet references.

ASSOCIATION: Institut elementoorganicheskikh soyedineniy AN SSSR
(Institute of Elemental Organic Compounds AS USSR)

SUBMITTED: December 1, 1960

Table 1. Degradation of poly(fluorophenylene)ethyl by phenyl fluoride.
Legend: (I) Weight ratio of phenyl fluoride to poly(fluorophenylene)ethyl;
(II) obtained, % of the initial substances; (III) of low-molecular
reaction products; (IV) of poly(fluorophenylene)ethyl; (V) molecular weight
of the polymer.

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Synthesis of polyarylenealkyls...

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B124/B101

Table 2. Degradation of poly(fluorophenylene)ethyl by phenyl fluoride.
Legend: (I) Weight ratio of aluminum chloride to poly(fluorophenylene)ethyl;
(II) yield, % of the initial substances; (III) of low-molecular reaction
products; (IV) of poly(fluorophenylene)ethyl; (V) molecular weight of the
polymer.

Table 3. Degradation of poly(fluorophenylene)ethyl by phenyl fluoride
(molecular weight of the initial polymer: 3250). Legend: (I) Reaction
time, hr; (II) obtained, % of the initial substances; (III) of low-
molecular reaction products; (IV) of poly(fluorophenylene)ethyl;
(V) molecular weight of the polymer. X

Card 4/4

15.8150 2209

29735
S/190/61/003/011/004/016
B124/B101

AUTHORS: Korshak, V. V., Fedorova, L. S., Kolesnikov, G. S.

TITLE: Synthesis of polyarylenealkyls. XII. Polycondensation of 1,2-dichloroethane with phenyl bromide

PERIODICAL: Vysokomolekulyarnyye soyedineniya, v. 3, no. 11, 1961, 1650-1654

TEXT: Polycondensates of 1,2-dichloroethane with phenyl bromide were prepared in the presence of $AlCl_3$ using the same method as that described by the authors in Refs. 1 (Izv. AN SSSR, Otd. khim. n., 1955, 359) and 2 (Izv. AN SSSR, Otd. khim. n., 1958, 53) except that dibromodiphenyl ethane and diphenyl ethane were distilled off in vacuo after driving off the solvent and after conclusion of the reaction. The molecular weight of the polymer obtained was determined viscosimetrically, and the constant K_m

in the Staudinger equation was assumed to be equal to $1.8 \cdot 10^{-4}$. With decreasing phenyl bromide excess in the reaction mixture, both the molecular weight and the yield of polycondensation products are increased; maximum values are obtained with a phenyl bromide - dichloroethane ratio

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B124/B101

Synthesis of polyarylenealkyls...

of 0.95. When phenyl bromide - dichloroethane ratios of 1.2 and less are used, three-dimensional products are formed. The bromine content was 28.7 % in soluble poly(bromophenylene)ethyl and 21.5 % in the three-dimensional polycondensation product, while the theoretical bromine content is 43.7 %. This circumstance is attributed to the fact that migration of bromine takes place during polycondensation which leads to the formation of an inhomogeneous, halogen-substituted polymer. The yields of polymers (Fig. 1) and the molecular weights (Fig. 2) of the polycondensates of dichloroethane with phenyl chloride, fluoride, and bromide, respectively, decrease in the order: phenyl fluoride > phenyl chloride > phenyl bromide which is due to the fact that steric hindrance increases with the size of the halogen substituent. Optimum catalyst concentration of 8 mole% with respect to maximum molecular weight of poly(bromophenylene)ethyl was established (Table 2). The low-molecular reaction products were rectified to yield two fractions, one of which was identified to be dibromodiphenyl ethane and the other to be diphenyl ethane. It was shown by structural analysis by means of destructive oxidation with chromosulfuric acid that, due to partial conversion of the phenyl bromide to benzene which takes part in polycondensation, a copolymer forms in the course of the relative

2

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Synthesis of polyarylenealkyls...

29735
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B124/B101

polycondensation. There are 2 figures, 2 tables, and 6 references:
3 Soviet and 3 non-Soviet.

ASSOCIATION: Institut elementoorganicheskikh soyedineniy AN SSSR
(Institute of Elemental Organic Compounds AS USSR)

SUBMITTED: December 1, 1960

Fig. 1. Influence of the phenyl halide - dichloroethane ratio on the yield of polymer and low-molecular fractions: (1), (2), (3) yield of polymer; (1a), (2a), (3a) yield of low-molecular products; (1), (1a) phenyl fluoride; (2), (2a) phenyl chloride; (3), (3a) phenyl bromide.
Legend: (A) Yield, %; (B) phenyl halide - dichloroethane ratio.

Fig. 2. Influence of the phenyl halide - dichloroethane ratio on the molecular weight of the polymer. (1) benzene; (2) phenyl fluoride; (3) phenyl chloride; (4) phenyl bromide. Legend: (A) Molecular weight; (B) phenyl halide - dichloroethane ratio.

Card 3/3

29736

S/190/61/003/011/005/016
B124/B101

15.5540

7209

AUTHORS: Korshak, V. V., Mozgova, K. K., Shkolina, M. A.

TITLE: Synthesis of graft copolymers. VIII

PERIODICAL: Vysokomolekulyarnyye soyedineniya, v. 3, no. 11, 1961, 1655-1660

TEXT: Results obtained when styrene is grafted to heat-activated caprone fiber are given in this paper. The effect of the time of thermal treatment of the fiber on the yield of grafted polystyrene is studied at temperatures ranging from 80 to 150°C in a nitrogen stream and in air (Fig. 1). Up to 20 min from the beginning, active centers of copolymerization of the fiber with styrene are formed at 80°C in nitrogen, with no further oxidation of the fiber occurring on heating. When kept at a constant temperature of 80°C in air, two maxima appear, the first of which is due to the presence of active centers prior to heat treatment, and the second to the secondary formation of active groups by oxidation. From data given in Fig. 1 it can be further concluded that the yield of grafted polystyrene increases with the time of copolymerization, and that the formation of active centers in the fiber is accelerated by a temperature rise. Maximum yield of graft

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Synthesis of graft copolymers. VIII

copolymer is obtained when the fiber is kept at 110°C in a thermostat for 3 min, with true temperature in the thermostat and, thus, also of the sample being about 90°C. From measured viscosity values of the graft copolymers, optimum results were obtained under the same conditions as mentioned (Table 1). A polystyrene layer can be grafted to the caprone fiber with yields up to 30% and a molecular weight up to 60,000-80,000 (Table 2). It is shown that the described grafting takes place essentially on the surface of the polymer. A. P. Zasechkina and A. I. Volkova took part in experimental work. There are 3 figures, 2 tables, and 5 references: 4 Soviet and 1 non-Soviet. The reference to the English-language publication reads as follows: A. J. Goldberg, W. P. Hohenstein, H. Mark, J. Polymer Sci., 2, 503, 1947.

ASSOCIATION: Institut elementoorganicheskikh soyedineniy AN SSSR
(Institute of Elemental Organic Compounds AS USSR)

SUBMITTED: December 7, 1960

Card 2/2

15.8150

30911
S/190/61/003/012/005/012
B101/B110

AUTHORS: Korshak, V. V., Rogozhin, S. V., Volkov, V. I.

TITLE: Investigations in the field of coordination polymers. VIII. Polymers on the basis of aromatic, o,o'-dihydroxydicarboxylic acids and bivalent metals

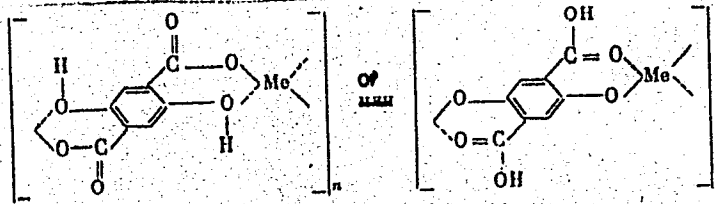
PERIODICAL: Vysokomolekulyarnyye soyedineniya, v. 3, no. 12, 1961, 1808 - 1815)

TEXT: The authors deal with the synthesis of high-molecular compounds in which metal atoms are combined with the organic part of the macromolecule by means of coordination bond. The present investigation describes the interaction of acetyl acetonates, acetates, and chlorides of Cu, Zn, Ni, Co, Cd, and Be with 2,5-dihydroxy terephthalic acid (I) and 4,4'-dihydroxy triphenyl methane-3,3'-dicarboxylic acid (II), also their dimethyl esters (III) and dimethoxy derivatives (IV). In the reaction of I with acetyl acetonates of Zn, Ni or Cu in dimethyl formamide, acetyl acetone was freed, and polymers containing metal were formed, for which the structural formulas

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B101/B110

Investigations in the field...



are suggested. The polymer with Zn decomposes at 359°C, the polymer with Cu at 253°C. The reaction of II with Zn or Cu compounds (acetylacetonates and acetates) in methyl formamide (some tests also in methanol or water) resulted in insoluble, nonfusible substances which decomposed above 350°C. II was obtained by condensation of salicylic acid with benzaldehyde in acid medium at 85°C. In order to study the role of carbonyl and hydroxyl oxygen, III and IV were synthesized. III was obtained by esterification of II by means of methanol in the presence of H₂SO₄, IV by treating the disodium salt of II with dimethyl sulfate. Since III and IV melted without decomposition, polymerization could also be achieved in the melt by means of these substances. Reaction of III with Co, Ni, Cu, and Zn compounds resulted in insoluble, nonfusible substances for which formula

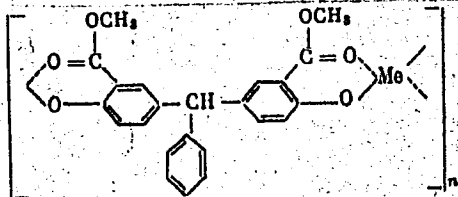
Card 2/4

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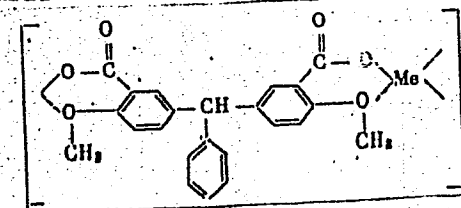
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B101/B110

Investigations in the field...



is suggested. The composition of the Cu and Zn compounds was not according to theory. This is ascribed to by-reactions. Reaction of IV with Zn- or Be acetate in acetic acid (>130°C), and of the dipotassium salt of IV with CuCl₂, BeCl₂, ZnCl₂, and CdCl₂ in H₂O led to polymers which changed considerably at 250 - 450°C, with the stability decreasing in the order Be > Zn > Cd > Cu. The structural formula



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B101/B110

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is suggested. The compounds obtained from aqueous solution deviated in their composition from the theoretical composition, probably due to water content. The considerable increase in volume of the Be and Zn compounds above 200°C is ascribed to continuation of the incomplete chemical reaction at elevated temperature. In the esters of aromatic o-hydroxy acids, carbonyl oxygen of the carboxyl group effects the formation of the coordination bond. In o-methoxy acid, the oxygen of the methoxy group has an effect. All polymers were colored powders. The polymers obtained from the melt had a composition which came nearest to theory. There are 1 figure, 6 tables, and 15 references: 9 Soviet and 6 non-Soviet. The four most recent references to English-language publications read as follows: S. Kanda, Y. Saito, Bull. Chem. Soc. Japan, 30, 192, 1957; H. Kling, L. Alexander, G. Summer, Acta crystallogr., 11, 41, 1958; R. G. Charles, M. A. Pawlikowski, J. Phys. Chem., 62, 440, 1958; J. Wilkins, E. Wittbecker, US Patent 2659711, 1953.

ASSOCIATION: Institut elementoorganicheskikh soyedineniy AN SSSR
(Institute of Elemental Organic Compounds AS USSR)

SUBMITTED: January 6, 1961
Card 4/4

KORSHAK, V.V.; VINOGRADOVA, S.V.

Polyarylates. Usp. khim. 30 no. 4:421-461 Ap '61. (MIRA 14:4)

1. Institut elementoorganicheskikh soyedineniy AN SSSR.
(Esters) (Polymers)

20638

15.9207

2209 also 1043, 1143, 1138

S/020/61/136/006/014/024
B103/B203

11.2210

AUTHORS:

Kerzhak, V. V., Corresponding Member AS USSR, Kasatochkin, V.I.,
Sladkov, A. M., Kudryavtsev, Yu. P., and Usenbayev, K.

TITLE:

Synthesis and properties of polyacetylene

PERIODICAL:

Doklady Akademii nauk SSSR, v. 136, no. 6, 1961, 1342-1344

TEXT: The authors produced polyacetylene (PA) and studied its chemical structure and physical properties. They assumed that PA formed in the oxidation of bis-acetylene acetylenides of the type $\text{HC}\equiv\text{C}-(\text{CH}_2)_n-\text{C}\equiv\text{CH}$

which are said to be among the polymeric products not yet studied. They had already suggested a formation mechanism of PA in Ref. 3. In the present investigation, they produced the required acetylenide by passing acetylene through the ammoniacal solution of a salt of bivalent copper. Subsequently, the acetylenide was oxidized by an aqueous solution of potassium ferricyanide at boiling temperature. The authors assumed that the resulting black powder (containing 98% of C) was a mixture of polymer homologs of polyacetylene. On the basis of the temperature-dependent weight losses

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Synthesis and properties of...

(Fig. 1) and the electron paramagnetic resonance, they conclude that this product is a polymer with cumulene structure, probably $H-(C=C=C=C)_n-H$.

PA showed high heat resistance, being transformed into graphite only at 2300°C. Below 2300°C, the carbon in PA remains in the form of polyacetylene. Graphite is also formed by long boiling of annealed PA samples in concentrated HCl. The authors point to the readiness of transformation of carbon atom chains of PA into graphite monolayers, and the corresponding transformation of valence forms under the action of HCl. The electric resistivity ρ measured by the zero method on an MTB(MTV) bridge dropped with rising temperature. This is explained by the concentration of crystalline copper due to thermal dissociation and the separation of terminal copper atoms from PA. ρ continued dropping at higher temperatures when copper had already evaporated and no graphite was formed. This indicated an extension of PA chains during the pyrogenetic synthesis which took place due to thermal dissociation and copper separation, as well as subsequent recombination of the resulting free polymeric radicals. The emf α was measured by the compensation method on a PNTB (PPTV) high-resistance potentiometer. On the basis of the values obtained for ρ and α , the authors

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conclude that the PA sample investigated is an n-type semiconductor. The copper atoms imbedded in the molecular carbon chain with polyallene structure play the role of the electron donor. This is confirmed by the fact that the α of PA samples which were produced with the use of stronger copper-free oxidizers (nitrate ion, H_2O_2) is equal to zero. The change of the sign of α (near zero at 1300 and 1500°C + above 1500 up to 2300°C corresponds to the transition of the PA sample to a p-type semiconductor. The authors think that this is coupled with the thermal dissociation and the separation of copper- and hydrogen atoms from the carbon chain, and is certainly connected with the acceptor properties of the terminal C atoms. There are 3 figures, 1 table, and 3 references: 1 Soviet-bloc and 1 non-Soviet-bloc.

ASSOCIATION: Institut goryuchikh iskopayemykh Akademii nauk SSSR
(Institute of Mineral Fuels of the Academy of Sciences USSR)
Institut elementoorganicheskikh soyedineniy Akademii nauk
SSSR (Institute of Elemental-organic Compounds of the
Academy of Sciences USSR)

Card 3/5

15.8114 2209

24.3600 (1035, 1138, 1482)

S/020/61/137/006/013/020
B103/B217

AUTHORS: Nesmeyanov, A. N., Academician, Korshak, V. V., Corresponding Member AS USSR, Voyevodskiy, V. V., Corresponding Member AS USSR, Kochetkova, N. S., Sosin, S. L., Materikova, R. B., Bolotnikova, T. N., Chibrikov, V. M., and Bazhin, N. M.

TITLE: Synthesis and some optical-magnetic properties of polyferrocenes

PERIODICAL: Doklady Akademii nauk SSSR, v. 137, no. 6, 1961, 1370-1373

TEXT: The authors studied the magnetic properties of ferrocene derivatives: 1) of the polyferrocenylenes (Table 1, nos. 1-6), 2) the polydiisopropylferrocene (Table 1, nos. 7-8), 3) the polymethano- and 4) the polyethanopolyferrocenes (Table 1, nos. 9-13). They were synthesized by: A) Polyrecombination. To 1) and 2). 1 mole ferrocene (or of its diisopropyl homolog) was treated with 1 mole tertiary butyl peroxide in nitrogen atmosphere at 200°C. 1) and 2) are assumed to be formed as follows: the Butoxyl and methyl radicals formed during peroxide decomposition separate the hydrogen from ferrocene (or the α -hydrogen). The radicals thus formed

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Synthesis and some ...

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recombine and form linear 1) or 2), easily soluble in benzene. An insoluble polymer (Table 1, nos. 5-6) with a two- or tridimensional network structure is formed simultaneously. The conversion of ferrocene to high-molecular products amounted to 25%. Nos. 1-3 have a softening temperature of 290-300°C and are a dark-red powder, whereas nos. 5-6 had their softening temperature at about 400°C and were light-yellow. B) Polyalkylation of ferrocene by methylene chloride and 1,2-dichloroethane in the presence of anhydrous aluminum chloride. Aluminum chloride solution in 50 ml of dihalogen alkane was added gradually to 40 g ferrocene dissolved in 250 ml dry dihalogen alkane. The mixture was stirred for 6 hr at the boiling temperature of the solvent. The next day, 10 g aluminum chloride in 25 ml dihalogen alkane were added and treated for 6 hr as above. The mixture was decomposed by ice and HCl and treated with sodium sulfite. The obtained 3) and 4) were well soluble in benzene, differed, however, by their solubility in ether. Table 1 shows the molecular weights, the always equal g-factor and the magnetic characteristics of all substances produced. The decomposition temperature of 9-13 was 115-120°C. All substances are amorphous powders, nos. 9 and 10 light-yellow, no. 11 grey-brown. Nos. 10 and 11 are of a chemical composition similar to that of no. 9 (pentaethanodiferrocene).

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B103/B217

Synthesis and some ...

They consist possibly of 2 and 4 molecules similar to the latter, connected by ethane bridges. 4-5 methylenes in the molecule of nos. 12 and 13 belong to 2 ferrocene radicals. They do not contain halogen. The infrared spectra of nos. 9-13 have frequencies within the range $1000-1100\text{ cm}^{-1}$. To 1). Derivatives 1) having a π -conjugation between the ferrocene links give a signal the electron paramagnetic resonance (e-p-r), similarly to the poly-aromatic hydrocarbons. This cannot be explained by the presence of a corresponding quantity of the oxidized form of the ferricinium cation. Table 1 shows that also polymers in which the ferrocene links are separated by the $-\text{CH}_2-\text{CH}_2-$ group give an e. p. r. signal. It is known that the delocalization of the unpaired electrons between the two phenyl rings is not prevented by this group. In the substances described here, which give an e. p. r. signal, this signal is the smaller, the smaller the number of ferrocene links is. This signal vanishes in 2). Polymers with a low molecular weight give no e. p. r. signal in the solution (benzene), but in solid state. This is explained by the fact that the intramolecular interactions cause in solid state a conjugation of the adjacent polymer molecules. This causes for its part an e. p. r. signal. All polymers

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Synthesis and some

giving this signal show a single symmetrical line of the e. p. r. of the Lorenz type. The 1) obtained from the reaction A yields a wide e. p. r. line of 120-160 oersteds, its width being dependent on the polymer structure. This line becomes broader on reducing the measuring temperature. Its width is changed most considerably in low-molecular polymers. The authors believe the nature of the measured signals to be unclarified, they cannot maintain that the number N of the unpaired electrons per 1 member, determined by a comparison with the standard, corresponds to their actual number. N may, however, be a certain characteristic of the magnetic properties of the system. (nos. 2-4). N reaches an anomalous size in the insoluble polymer no. 5. This is assumed to be connected with a collective effect of the ferromagnetic type. The ultraviolet (UV-) spectra of 1) dissolved in n-octane, which give an e. p. r. signal in solid state, differ from the ultraviolet spectra of such that give no signal in solid state. In the first case the UV-spectrum agrees completely with that of ferrocene dissolved in CCl_4 . It was proved for these spectra (Ref. 7) that the charge transfer takes place here under formation of an ion pair $\text{Fer}^+\text{CCl}_4^-$. On the contrary, the UV-spectrum of such 1) that give no e. p. r. signal is similar

Card 4/65

15. 8150

11. 2219

25339
S/020/61/138/006/015/019
B103/B215

AUTHORS: Korshak, V. V., Corresponding Member AS USSR, and
Vinogradova, S. V.

TITLE: Some laws of the polycoordination reaction

PERIODICAL: Akademiya nauk SSSR. Doklady, v. 138, no. 6, 1961, 1353-1356

TEXT: The authors determined the conditions for the synthesis of coordination polymers with a molecular weight of more than 100,000. The tetra-ketone 4,4'-bis-(acetoacetyl)-phenyl ether (BAPE) was used as initial ligand, since solubility of the final product is of great advantage for the examination. The authors allowed BAPE to react with beryllium- and zinc acetoacetates and also with zinc acetate. Polycoordination in some respects reminds of polycondensation. In both cases, the polymer is synthesized due to the interaction between two types of reactive groups where, besides the growth of polymer chains, low-molecular products are separated: in the former case water, alcohol, etc., in the latter case acetylacetone, acetic acid, etc. The authors had already found polycondensation to be a balanced process. If the low-molecular product is

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Some laws of the polycoordination reaction

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B103/B215



removed from the reaction sphere, the equilibrium may shift and thus increase the polymer yield by favoring the formation of polymer molecules. The authors found that polycoordination like polycondensation is a reversible process, and that coordination polymers are completely destroyed by the low-molecular reaction product. They also proved that coordination polymers react with chemically similar substances. The low-molecular product should therefore be completely removed from the reaction sphere. The reaction was conducted (a) in a solution, (b) in a melt. Ad (a): BAPE and zinc acetate dissolved in dimethyl formamide were subjected to polycoordination in nitrogen flow at 120 and 140°C. In both cases, the polymer yield was 84-87 % after 5 hr. The intrinsic viscosity of the polymer in cresolic solution was 0.06-0.09 and remained constant during a reaction time of 0.5-11 hr. In their attempts to increase the viscosity by higher reaction temperatures (dissolution in dilyn at 220°C for 5 hr), the authors obtained a polymer poorly soluble in cresol. Therefore they continued their experiments with beryllium polymers (instead of zinc) in dilyn at 200-240°C. Thus, they found that polymers of higher viscosity are formed in solutions of higher concentration (0.74 to 2.00 mole/l). Distillation of acetylacetone also favors the increase in

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Some laws of the polycoordination reaction

molecular weight. The quantitative ratio of the initial products also has a great effect upon viscosity. A polymer of the highest molecular weight forms at an equimolar ratio of the two components. A 0.2 mole excess of one component reduces the viscosity almost to 1/4. If the excess is higher, viscosity is no longer affected. Ad (b): In the melt, BAPE and beryllium form a polymer with a viscosity of 0.06 already within the first hour at 200°C. It remains constant during 5 hr of reaction. At 260°C, viscosity is doubled and increases at this temperature as the time of reaction increases. In vacuo (1-2 mm Hg), the maximum increase in viscosity is reached in the second stage of reaction. Thus, the authors obtained a viscosity of 0.44 of the coordination polymers by conducting the reaction first in nitrogen flow for 5 hr at 200°C, then in vacuo for another 5 hr at 260°C. When using 6 g of BAPE instead of 0.5 g, a viscosity of 0.48 was obtained in vacuo at a reaction time of 14 hr and 260°C. The fractionation of this polymer from chloroform with n-hexane yielded three fractions: (I) 27.3 % (molecular weight: 12600), (II) 28.2 %, and (III) 44.5 %, with a viscosity in chloroform of 1.2, 0.5, and 0.32, respectively. The authors explain the increase of the molecular weight by the above equilibrium character of the process. The removal of

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B103/B101

IS 8170

2209

AUTHORS: Polyakova, A. M., Korshak, V. V., Corresponding Member AS USSR, Vdovin, V. M., and Tambovtseva, Ye. S.

TITLE: Study of the polymerization of cyanogenous organosilicon compounds

PERIODICAL: Akademiya nauk SSSR. Doklady, v. 141, no. 3, 1961, 641-644

TEXT: The polymerizability of cyanogenous alkenyl silane derivatives was studied. These compounds were polymerized (a) under pressure (6000 atm) in the presence of the radical initiators (1) azoisobutyrodinitrile, (2) tert-butyl peroxide, or (3) benzoyl peroxide; (b) at normal pressure with Pt/C or $H_2PtCl_6 \cdot 6H_2O$ as catalysts. It was found that cyano-isopropoxy alkenyl silane derivatives polymerize at comparatively low temperature. Above $120^{\circ}C$ these compounds frequently decompose. Only under the conditions of (a) colorless polymers were obtained at $80^{\circ}C$. For the rest, they were yellow to brown. Some of the experiments ended up with explosive polymerization and charring of the products. Most of the products are slightly soluble (Table 1, nos. 1-22). The authors also

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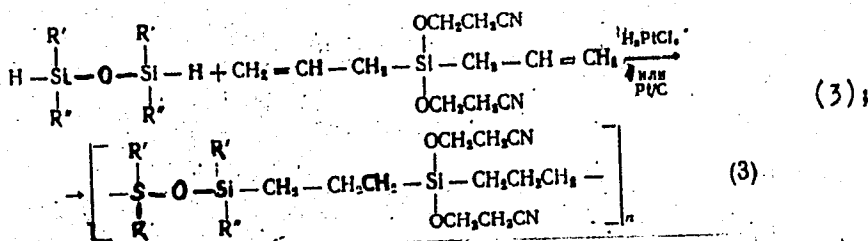
Card 1/3

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B103/B101

Study of the polymerization ...



(1) = or. There are 1 table and 9 references: 7 Soviet and 2 non-Soviet. The two references to English-language publications read as follows: J. C. Williams, R. A. Pike, F. Fekete, Ind. and Eng. Chem., 51, 939 (1959); R. M. Savage, Rubber Age, 84, 975 (1959).

ASSOCIATION: Institut elementoorganicheskikh soyedineniy Akademii nauk SSSR (Institute of Elemental Organic Compounds of the Academy of Sciences USSR). Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR (Institute of Organic Chemistry imeni N. D. Zelinskiy of the Academy of Sciences USSR) X

Card 3/03

ANDRIANOV, Kuz'ma Andrianovich; KORSHAK, V.V., otv. red.; ZHDANOV, A.A., red.; BALLOD, A.I., tekhn. red.; DOROKHINA, I.N., tekhn. red.

[Polymers with inorganic main chains of molecules] Polimery s neorganicheskimi glavnymi tsepiami molekul. Moskva, Izd-vo Akad. nauk SSSR, 1962. 326 p. (MIRA 16:2)

1. Chlen-korrespondent Akademii nauk SSSR (for Korshak).
(Silicon organic compounds) (Polymers)
(Organometallic compounds)

PHASE I BOOK EXPLOITATION

SOV/6119

Korshak, Vasilii Vladimirovich, and Tat'yana Mikhaylovna Frunze

Sinteticheskiye geterotsepnnyye poliamidy (Synthetic Hetero-Chain Polyamides). Moscow, Izd-vo AN SSSR, 1962. 523 p.
Errata slip inserted. 5000 copies printed.

Sponsoring Agency: Akademiya nauk SSSR. Institut elementoorganicheskikh soyedineniy.

Resp. Ed.: S. R. Rafikov, Doctor of Chemical Sciences; Eds.: V. M. Zhulin and I. P. Loskutova; Tech. Ed.: S. G. Tikhomirova.

PURPOSE: This book is intended for scientific research workers, students and teachers at schools of higher technical education, and technicians in the synthetic fiber, paint, plastics, and other industries which produce or utilize polyamides.

COVERAGE: The monograph gives a comprehensive summary of the literature through 1959, and a selection of the more interesting materials published in 1960, on the chemistry and physics of hetero-chain polyamides. Types of polyamides, polymerization, the mechanics of polycondensation, and the chemical and physical

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Synthetic Hetero-Chain Polyamides

SOV/6119

properties and the production of polyamides are discussed. References are given following each chapter (Chs. VII and VIII each have a bibliography of over 700 items). Altogether about 400 Soviet and 1500 non-Soviet authors are cited. No personalities are mentioned.

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Card 4/5

KORSHAK, V. V.

PHASE I BOOK EXPLOITATION

SOV/6034

Konferentsiya po khimii i primeneniyu fosfororganicheskikh soyedineniy. 2d, Kazan', 1959.

Khimiya i primeneniye fosfororganicheskikh soyedineniy; trudy (Chemistry and Use of Organophosphorus Compounds; Conference Transactions) Moscow, Izd-vo AN SSSR, 1962. 630 p. Errata slip inserted. 2800 copies printed.

Sponsoring Agency: Akademiya nauk SSSR. Kazanskiy filial.

Resp. Ed.: A. Ye. Arbuzov, Academician; Ed. of Publishing House: L. S. Povarov; Tech. Ed.: S. G. Tikhomirova.

PURPOSE: This collection of conference transactions is intended for chemists, process engineers, physiologists, pharmacists, physicians, veterinarians, and agricultural scientists.

COVERAGE: The transactions include the full texts of most of the scientific papers presented at the Second Conference on the Chemistry and Use of

Card 1/14

Chemistry and the Use of Organophosphorus (Cont.)

SOV/6034

Organophosphorus Compounds held at Kazan' from 2 Nov through 1 Dec 1959. The material is divided into three sections: Chemistry, containing 67 articles; Physiological Activity of Organophosphorus Compounds, containing 26 articles; and Plant Protection, containing 12 articles. The reports reflect the strong interest of Soviet scientists in the chemistry and application of organophosphorus compounds. References accompany individual reports. Short summaries of some of the listed reports have been made and are given below.

TABLE OF CONTENTS:[Abridged]:

Introduction (Academician A. Ye. Arbuzov) 3

TRANSACTIONS OF THE CHEMISTRY SECTION

Gefter, Ye. L. [NII plastmass (Scientific Research Institute of Plastics, Moscow)]. Some Prospects for the Industrial Use of Organophosphorus Compounds 46

Card 2/14

Chemistry and the Use of Organophosphorus (Cont.)

SOV/6034

triorganosilanols (R_3SiOH) with acids of phosphorus under conditions of azeotropic distillation of water in the presence of inert solvents. Another is based on the interaction of triorganosilanes with orthophosphoric and methylphosphonic acids in the presence of active colloidal nickel.

Korshak, V. V., I. A. Gribova, and M. A. Andreyeva [Institut elementoorganicheskikh soedineniy (Institute of Organoelemental Compounds, Academy of Sciences USSR, Moscow)]. Study of Phosphorus-Containing Compounds

242

The polycondensation of dichlorides of phosphonic acids with diols has been studied by following the interaction of methylphosphonic dichloride with hydroquinone in a nitrobenzene solution at a temperature of 140 to 170°C. The properties of polyesters of phosphonic acid have also been studied.

Card 4/14

Chemistry and the Use of Organophosphorus (Cont.)

SOV/6034

Korshak, V. V., T. M. Frunze, V. V. Kurashev, and L. V. Kozlov [Institute of Organoelemental Compounds]. Synthesis of Some Phosphorus-Containing Dicarboxylic Acids and Derivation of Polyamides Based on Such Acids

247

Phosphorus-containing dicarboxylic acids have been obtained by synthesis and used for the preparation of polyamides. The effect of the phosphorus and the structure of the acids on the properties of the polyamides has been studied.

Kolesnikov, G. S., Ye. F. Rodionova, and L. S. Fedorova [Institute of Organoelemental Compounds]. Synthesis, Polymerization, and Copolymerization of Esters of Vinylphosphonic Acid

255

The authors obtained esters of vinylphosphonic acid and demonstrated that these esters are capable of entering the polymerization and copolymerization reaction with other monomers. Polymers and copolymers of the dichloride and esters of vinylphosphonic acid have been synthesized and their properties determined.

Card 5/14

Chemistry and the Use of Organophosphorus (Cont.)

SOV/6034

Andreyeva, M. A., I. A. Gribova, M. I. Kabachnik, G. S. Kolesnikov, V. V. Korshak, T. Ya. Medved', Yu. M. Polikarpov, Ye. F. Rodionova, and L. S. Fedorova [Institute of Organoelemental Compounds]. Some Methods of Synthesis of New Organophosphorus Monomers and Polymers

263

This study attempts to develop new methods of synthesis of organophosphorus monomers and polymers for obtaining high-molecular fireproof materials. The authors synthesized vinyl compounds of pentavalent phosphorus and studied their properties, as well as those of the polymers obtained.

Moshkin, P. A., Ye. L. Getter, and I. K. Rubtsova [Scientific Research Institute of Plastics]. Study of the Synthesis and Uses of Some Organophosphorus Compounds in the Plastics Industry

279

Industrial methods for the preparation of esters of phosphoric acid and for testing qualities of these acids as plasticizers have been developed, along with methods for obtaining phosphorus-containing monomers for use in polymerization, copolymerization, and polycondensation reactions. Polyesters based on dichlorides of

Card 6/14

15.8112

32358
S/191/62/000/001/002/006
B145/B110

AUTHORS: Korshak, V. V., Akutin, M. S., Vinogradova, S. V.,
Rodivilova, L. A., Valetskiy, P. M., Lebedeva, A. S.,
Salazkin, S. N.

TITLE: Polyarylates - new thermostable polymers

PERIODICAL: Plasticheskiye massy, no. 1, 1962, 9-13

TEXT: A survey of the properties of polyarylates is given. They are best synthesized from bifunctional phenols and dicarboxylic acid chlorides. Some of the synthesized polyarylates and their softening temperatures are given in Table 1. The great number of rings in the polymer ensure high resistance to most organic solvents as well as to gasolines and oils. At room temperature, the polyarylate VA (ID) is stable against H_2O_2 , dilute and concentrated caustic soda solutions, acetic acid, formic acid, nitric acid, and sulfuric acid. The effect of dilute and concentrated ammonia solutions considerably reduces the molecular weight of ID. Polyarylates on the basis of phenolphthalein are readily soluble in a number of solvents, which facilitates the production of foils. At the NIIPM it was
Card 1/3

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B145/B110

Polyarylates - new thermostable ...

established that the polyarylates TA (TD) and ID withstand high temperatures. Decomposition increases with rising temperature, at first slowly and then sharply at about 400°C. The oxidation of ID sets in at 250°C and proceeds slowly. Measurement of breakdown voltage, temperature dependence of tan δ, dielectric constant, and volume resistivity for some polyarylates prove that they are better dielectrics than polyethylene terephthalate, polycarbonate, etc. Polyarylates have good mechanical properties at various temperatures. Working processes are being elaborated at present. Specimens of mixed polyarylates were obtained by pressure casting, the tensile strength of which reached 850 kp/cm². Specimens sprayed on metal showed an adhesion to metal of 75 to 150 kp/cm². Work is also in progress on polyarylates with double bonds and free functional groups. They might be used as a basic material for the production of varnishes, glues, glass-reinforced plastics, and foam plastics. There are 5 figures, 6 tables, and 5 Soviet references.

Table 1. Softening temperature of polyarylates of different structures.
Legend: (1) polyarylate; (2) structure of the chain link; (3) softening temperature in °C; (4) TD; (5) ID; (6) TG; (7) IG; (8) TR; (9) IR; (10) TF; (11) IF; (12)-(14) ITD; (15) IDR; (16) TDR; (17) IFD; (18) IAD; * the
Card 2/3

32358

S/191/62/000/001/002/006

B145/B110

Polyarylates - new thermostable ...

molecular ratio of the initial dicarboxylic acid chlorides related to 1 mole of diol is given in parentheses; * * the molecular ratio of the initial diols related to 1 mole of dicarboxylic acid chloride is given in parentheses.

Card 3/3

x

34946

S/191/62/000/003/004/010
B101/B147

15, 2170

AUTHORS: Kamenskiy, I. V., Sanin, I. K., Korshak, V. V.

TITLE: Polymers based on silicon-containing furan compounds.
Synthesis of esters of furfuryl alcohol and ortho-silicic acid

PERIODICAL: Plasticheskiye massy, no. 3, 1962, 8-12

TEXT: (1) The synthesis of tetrafurfuryl oxysilane (I) in the presence of KOH by alcoholysis of tetraethoxy silane (TES) with furfuryl alcohol is described. To avoid resinification, the alcohol is first only mixed with half the TES, after evaporation of 20% of the theoretical C_2H_5OH amount with the next quarter, and after evaporation of 35% C_2H_5OH with the rest. ✓

The reaction is continued until evaporation of 75% C_2H_5OH at 115-140°C.

The yield is 80-82%, the substance consists of yellowish crystals, m.p. 38-39°C, b.p. 204-206°C (4 mm Hg), d_4^{20} 1.231, n_D^{20} 1.5025. A by-product is the hitherto unknown ethoxy trifurfuryl oxysilane, a yellowish liquid, b.p.

Card 1/4

S/191/62/000/003/004/010
B101/B147

Polymers based on silicon- ...

152-154°C (1 mm Hg), d_4^{20} 1.1400, n_D^{20} 1.4890. (2) Synthesis of I by esterification of SiCl_4 with furfuryl alcohol. SiCl_4 is added dropwise to alcohol dissolved in benzene, excess pyridine is admixed as HCl acceptor. Pyridine hydrochloride was separated (a) by washing, dehydration of the benzene layer by CaCl_2 , distillation of I in vacuo, or (b), with higher yields (94%), by filtering off the pyridine hydrochloride. (3) Synthesis of tetrahydrofurfuryl orthosilicate (II) by alcoholysis of TES with tetrahydrofurfuryl alcohol in the presence of lead monoxide at 120-145°C for 4 hrs. The product (75% yield) was a heavy, colorless liquid, b.p. 215-216°C (1.5 mm Hg), d_4^{20} 1.1399, n_D^{20} 1.4680. (4) Synthesis of II by esterification of SiCl_4 , ratio SiCl_4 : tetrahydrofurfuryl alcohol : pyridine = 1.1 : 4 : 4.8, 4 hrs at 10°C, 80% yield referred to alcohol. (5) Synthesis of ethyl furfuryl oxysilanes by alcoholysis, similar to (1), of ethyl triethoxy silane or diethyl diethoxy silane with furfuryl alcohol during 5 hrs. The product was ethyl trifurfuryl ethoxy silane (54.5%), b.p. 159.5-160°C (1 mm Hg), d_4^{20} 1.1743, n_D^{20} 1.4988; and diethyl difurfuryl

Card 2/4

Polymers based on silicon ...

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B101/B147

oxysilane (48%), b.p. 138-139°C (3 mm Hg), d_4^{20} 1.0835, n_D^{20} 1.4845.

(6) Synthesis of alkyl(aryl)furfuryl oxysilanes by esterification of methyl, ethyl, or phenyl trichloro silane, dimethyl, diethyl dichloro silane, or trimethyl chloro silane with furfuryl alcohol, similar to (1). Products obtained: methyl trifurfuryl oxysilane (90%), b.p. 157-158°C (1 mm Hg),

d_4^{20} 1.1801, n_D^{20} 1.4992; dimethyl difurfuryl oxysilane, b.p. 102-103

(1 mm Hg), d_4^{20} 1.1021, n_D^{20} 1.4809; trimethyl furfuryl oxysilane (89%),

b.p. 39.0-39.5°C (1 mm Hg), d_4^{20} 0.9519, n_D^{20} 1.4449; ethyl trifurfuryl

oxysilane (91%), b.p. 159.5-160°C, d_4^{20} 1.1743, n_D^{20} 1.4988; diethyl
difurfuryl oxysilane (89%), b.p. 138-139°C (3 mm Hg), d_4^{20} 1.0835, n_D^{20} 1.4845;

and phenyl trifurfuryl oxysilane (59%), b.p. 199.5-200°C, d_4^{20} 1.2040,
 n_D^{20} 1.5358. (7) Esterification of methyl chlorosilanes with tetrahydro-

furfuryl alcohol produced (in 88-90% yields): methyl-tri-(tetrahydro-
furfuryl)-oxysilane, b.p. 179-181°C (2 mm Hg), d_4^{20} 1.1068, n_D^{20} 1.4648;

Card 3/4

Polymers based on silicon ...

S/191/62/000/003/004/010
B101/B147

dimethyl-di-(tetrahydrofurfuryl)-oxysilane, b.p. 123-125°C (1 mm Hg),
 d_4^{20} 1.0324, n_D^{20} 1.4505; and trimethyl-(tetrahydrofurfuryl)-oxysilane, b.p.
172-173°C (760 mm Hg), d_4^{20} 0.9214, n_D^{20} 1.4271. The infrared spectra of the
compounds are shown. Papers by Yu. K. Yur'yev (ZhOKh, 28, 3 (1958)) and
A. L. Mdzhoyan (DAN ArmSSR, 27, 305 (1958)) are mentioned. There are
7 figures, 1 table, and 25 references: 8 Soviet and 17 non-Soviet. The
four most recent references to English-language publications read as
follows: H. Olson, Ind. Eng. Chem., 47, 1411 (1955); K. Q. Wilks, J. Am.
Chem. Soc., 72, 1208 (1950); US Patent 2601497 (1952); US Patent 2569455,
C. A., 46, 3084 (1952). ✓

SUBMITTED: October 19, 1960

Card 4/4

3662

S/062/62/000/004/012/013
B110/B101

11.1340

AUTHORS: Korshak, V. V., Sladkov, A. M., and Luneva, L. K.

TITLE: Synthesis of elemental organic polymers with acetylene bonds in their chain

PERIODICAL: Akademiya nauk SSSR. Izvestiya. Otdeleniye khimicheskikh nauk, no. 4, 1962, 728

TEXT: New polymers were obtained by polycondensation of halides of elemental organic compounds, $RMeCl_2$, with Na acetylenides of bis-acetylenes in polar solvents (tetrahydrofuran, dimethyl ether, diethylene glycol, ethyl ether, etc.). The acetylenide was obtained from finely distributed sodium or sodium amide and bis-acetylene in the solvent. Elemental organic compounds in the same solvent were added at room temperature, heated to 60-100°C, filtered off, and the polymer was separated from the filtrate. Thus, the acetylenide was obtained from p-di-ethynyl benzene and sodium. After the addition of dimethyl dichloro silane, the substance was boiled for 7 hrs, cooled, and diluted with water. A light-yellow polymer not melting at

Card 1/2

Synthesis of elemental organic ...

S/062/62/000/004/012/013
B110/B101

300°C and slightly darkening at 240°C (C = 66.45, H = 7.74, Si = 20.92%) precipitated. The infrared spectra showed $C\equiv C$ (2250 cm^{-1}) and $Si-CH_3$ stretching vibrations (1250 cm^{-1}). The range of elastic deformation was thermodynamically determined at 150-300°C. Similarly, an acetylenide was obtained from phenyl acetylene and sodium. Addition of dimethyl dichloro silane at room temperature and subsequent boiling for 4 hrs yielded di-p-phenyl ethynyl dimethyl silane (b. p. 180-185°C at 4 mm Hg). In an analogous manner, polymers can also be obtained from other compounds of elements of Group IV. The resulting monomers were used for producing polymers and copolymers.

ASSOCIATION: Institut elementoorganicheskikh soyedineniy Akademii nauk SSSR (Institute of Elemental Organic Compounds of the Academy of Sciences USSR)

SUBMITTED: December 25, 1961

Card 2/2

KORSHAK, V.V.; KOMAROVA, L.I.; SIDOROV, T.A.

Infrared spectra of organic complexes of beryllium. *Izv. AN SSSR.*
Otd.khim.nauk no.5:813-815 My '62. (MIRA 15:6)

1. Institut elementoorganicheskikh sovedineniy AN SSSR.
(Beryllium organic compounds—Spectra)

KORSHAK, V.V.; KRONGAUZ, Ye.S.; BERLIN, A.M.

Organophosphorus polymers with P - N bonds. Izv. AN SSSR. Otd.
khim.nauk no.8:1412-1416 Ag '62. (MIRA 15:8)

1. Institut elementoorganicheskikh soyedineniy AN SSSR.
(Phosphorus organic compounds) (Polymers)

S/062/62/000/008/009/016
B101/B180AUTHORS: Korshak, V. V., Vinogradova, S. V., Salazkin, S. N., and Sidorov, T. A.

TITLE: Production of polyaryls based on phenol phthalein by interphase polycondensation

PERIODICAL: Akademiya nauk SSSR. Izvestiya. Otdeleniye khimicheskikh nauk, no. 8, 1962, 1416-1423

TEXT: This is the 47th report on heterochain polyesters. Interphase polycondensation of phenol phthalein (P) with chlorides of dicarboxylic acids yielded polymers of low intrinsic viscosity, $[\eta]$. Reacting P with isophthalic acid in this way in p-xylol solution, at initial reactant concentrations of 0.1 mole/l, with 2M NaOH per M phenol phthalein, resulted in $[\eta] \leq 0.23$ (in tricresol) and yields of up to 80%. Higher alkaline concentrations reduced both $[\eta]$ and yield. Nor did an emulsifier (Nekal) or catalyst (triethylbenzyl ammoniumchloride) cause an appreciable increase in $[\eta]$. Polycondensates from P and terephthalic acid (T), and mixed polycondensates from P, 4,4'-dihydroxydiphenylpropane

Card 1/3

Production of polyaryls based ...

S/062/62/000/008/009/016
B101/B180

(Dian) and I or T all had a low $[\eta]$ (0.26-0.32). $[\eta]$ was lower still (0.12-0.16) when the dichlorides of I and T were totally or partially replaced by fumaryl dichloride, due to the slight hydrolysis caused by the latter. These results are attributed to the slow rate of the tautomeric transformation of P. In alkaline solution it is assumed that there is equilibrium between the quinoid and the lactone forms. The chloride of the dicarboxylic acid only reacts with the lactone. Since transition from quinoid to lactone occurs slowly, hydrolysis of the acid chloride sets in, and the molecular weight remains low. This is supported by the absence of a band characterizing the quinoid structure at 1680 cm^{-1} in the IR spectra of the polycondensates. The 1300 cm^{-1} band, attributed by S. Lo Elisabeth to the quinoid form (Industr. and Engng. Chem., 52, 319 (1960)), was ascribed to the residue of I, since it was also observed in the polycondensate of Dian and I. The doublet $1710\text{-}1760\text{ cm}^{-1}$ is attributed to the different bonds of the carbonyl groups (ester and lactone bonds). There are 2 figures and 4 tables.

ASSOCIATION: Institut elementoorganicheskikh soyedineniy Akademii nauk SSSR (Institute of Elemental Organic Compounds of the Academy of Sciences USSR)

Card 2/3

Production of polyaryls based ...

S/062/62/000/008/009/016
B101/B180

SUBMITTED: February 17, 1962

Card 3/3

S/062/62/000/008/011/016
B117/B180

AUTHORS: Korshak, V. V., Kudryavtsev, R. V., Sergeyev, V. A., and
Itsikson, L. B.

TITLE: Investigation of hydrolytic polymerization mechanism of
 ϵ -caprolactam in the presence of water containing a heavy
oxygen isotope

PERIODICAL: Akademiya nauk SSSR. Izvestiya. Otdeleniye khimicheskikh
nauk, no. 8, 1962, 1468-1470

TEXT: In this investigation the water contained 6% O^{18} . ϵ -caprolactam
and the labeled water, in a 1:1.5 ratio, were heated for 6 hrs at $200^{\circ}C$.
The molecular weight of the resulting poly- ϵ -caproamide was relatively
low, and its O^{18} content the same as with an exchange reaction. From this
it is concluded that the monomer links on to the end groups of the
growing polymer chain during the reaction. When the polymer was heated
for 3 hrs at $250^{\circ}C$ in argon, the viscosity of the solution was found to
be higher than that of the initial polymer, (from $[\eta] = 0.38$ to $[\eta] = 1.76$),

Card 1/2

Investigation of hydrolytic ...

S/062/62/000/008/011/016
B117/B180

as also the molecular weight. In the final stage of the reaction, if all the water can be removed, polycondensation of the macromolecule will occur due to the reaction between amino and carboxyl end-groups. The course of the hydrolytic polymerization of ϵ -caprolactam described above confirms earlier predictions (V. V. Korshak and T. M. Frunze, Izv. AN SSSR. Otd. khim. n. 1955, 376). There is 1 table.

ASSOCIATION: Institut elementoorganicheskikh soyedineniy Akademii nauk SSSR (Institute of Elemental Organic Compounds of the Academy of Sciences USSR).

SUBMITTED: January 31, 1962

Card 2/2

KORSHAK, V.V.; ROGOZHIN, S.V.; VINOGRADOV, M.G.

Phthalocyanine polymers of diphthalyl ketone. Izv.AN SSSR.Otd.khim.
nauk no.8:1473-1475 Ag '62. (MIRA 15:8)

1. Institut elementoorganicheskikh soyedineniy AN SSSR.
(Ketone) (Phthalocyanine)

L0730

S/062/62/000/009/007/009
B119/B186

5.3832

AUTHORS: Korshak, V. V., Krongauz, Ye. S., and Gribkova, P. N.

TITLE: Production of a polymer by polyrecombination from diphenyl benzyl phosphine oxide

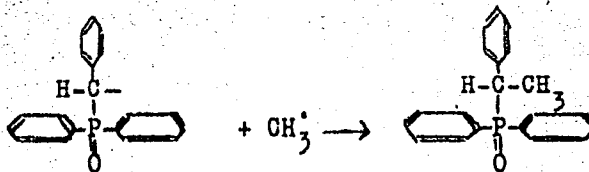
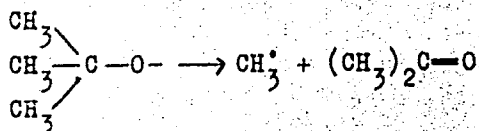
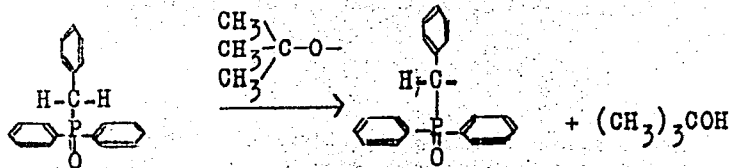
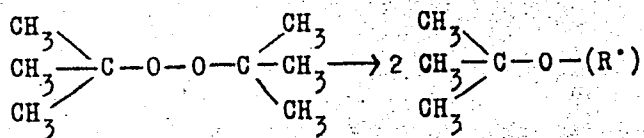
PERIODICAL: Akademiya nauk SSSR. Izvestiya. Otdeleniye khimicheskikh nauk, no. 9, 1962, 1638 - 1644

TEXT: $(C_6H_5)_2P(O)CH_2C_6H_5$ was polyrecombined by heating to 210 - 212°C in a current of N_2 and in the presence of tertiary butyl peroxide. The time of reaction (3 - 11 hrs) and the peroxide content (1 - 4 moles per 1 mole of diphenyl benzyl phosphine oxide (D)) were varied. A polymer with molecular weight between 33,000 and 35,000 was obtained. The melting point was 320 - 330°C, the specific viscosity of a 0.5 % solution in cresol < 0.1. The maximum polymer yield was 9.1 % referred to the amount of D used. Nothing certain could be learned as to the dependence of the yield on the mixing ratio D: peroxide or as to the time of reaction, or rate of peroxide admixture. The highly ramified polymer molecules are assumed to form according to the following reaction scheme:

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S/062/62/000/009/007/009
B119/B186

Production of a polymer by ...



Card 2/3

15,870

1,191h
S/191/62/000/011/006/019
B101/B186

AUTHORS: Akutin, M. S., Korshak, V. V., Rodivilova, L. A.,
Vinogradova, S. V., Budnitskiy, Yu. M., Valetskiy, P. M.,
Lebedeva, A. S.

TITLE: New data on processing and properties of polyarylates

PERIODICAL: Plasticheskiye massy, no. 11, 1962, 20-26

TEXT: This paper deals with experiments for determining the optimum processing conditions of polyarylates from isophthalic acid and diene (ID), terephthalic acid and diene (TD), and the mixed polymer ITD (ratio iso- to terephthalic acid 1:1). Preliminary experiments showed that the interfacial polycondensation in more concentrated solutions than hitherto usual gave polymers with low molecular weight: thus 13.5% by weight of diene in NaOH solution + 15-20% by weight of isophthalic dichloride in methylene chloride yielded a polymer with MW ~18,000. A better result was obtained for ITD in the presence of 1% triethyl benzyl ammonium chloride as catalyst: the reduced viscosity in tricresol was 0.58. Injection-molded products were made from ID, TD, and ITD, and tested. Results:

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New data on processing and ...

S/191/62/000/011/006/019
B101/B186

(1) At 280-360°C, ID and TD can be processed only in inert gas atmosphere since thermal destruction occurs if air is present. ITD can still be processed at these temperatures in the presence of air. (2) The strength of products depends on the molecular weight (or on the reduced viscosity). Adequate tensile strength ($\sim 400 \text{ kg/cm}^2$) is attained above $\eta_{\text{red}} = 1.0$. Products with a tensile strength of 850-900 kg/cm^2 were obtained from ITD with $\eta_{\text{red}} = 1.9-2.0$. (4) The tensile strength drops from 820 kg/cm^2 at 280°C to 480 kg/cm^2 at 340°C. (5) The effect of the molding time becomes manifest the tensile strength dropping from 850 kg/cm^2 after 10 min to 300 kg/cm^2 after 30 min molding time. (6) A change in molding pressure has no effect on the tensile strength. (7) Increasing the temperature of the mold from 80 to 160°C increases the tensile strength from 650 to 820 kg/cm^2 , but a further increase (to 200°C) reduces the tensile strength. (8) A study of the chemical stability of injection-molded specimens and films showed: good stability to mineral and organic acids, oxidants, and dilute alkalis; poor stability to concentrated alkalis, particularly ammonia; swelling in some solvents, injection-molded specimens being more stable than films. The chemical stability of polyarylates resembles that of polycarbonates, and is inferior to that of polyethylene terephthalate

Card 2/3

New data on processing and ...

S/191/62/000/011/006/019
B101/B186

only as regards the swelling in some organic solvents. There are
8 figures and 6 tables.

J

Card 3/3

42649

S/062/62/000/011/012/021
B101/B144

15.8080

AUTHORS: Korshak, V. V., Frunze, T. M., and Kozlov, L. V.

TITLE: Heterochain polyamides. Communication 32. Interfacial formation of mixed polyamides from mixtures of various diamines

PERIODICAL: Akademiya nauk SSSR. Izvestiya. Otdeleniye khimicheskikh nauk, no. 11, 1962, 2062 - 2069

TEXT: The rules governing the interfacial polycondensation of adipyl chloride (AC) with a mixture of ethylene diamine (I) and m-phenylene diamine (II), or I and hexamethylene diamine (III), were studied. Polyamides were also synthesized from sebacyl chloride (SC) and a mixture of III and piperazine (IV). The polycondensation was carried out at room temperature; the chloride was dissolved in benzene, the diamines in aqueous alkali. The molar ratio of the diamines was varied between 0:1 and 1:0. The relative reaction rate of II and III was determined by acylating their mixture with benzoyl chloride. The nitrogen content of the reaction product and its IR spectrum proved that mainly dibenzoyl hexamethylene amine was formed and that the reaction rate of III was consequently much higher

Card 1/3

Heterochain polyamides...

S/062/62/000/011/012/021
B101/B144

than that of II. In the polycondensation of AC with diamines the following were determined: the initial ratio K_1 of the diamines, the ratio K_2 of the diamines in the copolymer, and $\alpha = K_2/K_1$. The following values were

found: $K_1 = I/II$ $K_2 = I/II$ α $K_1 = I/III$ $K_2 = I/III$ α

4	0.54	0.14	4	2.03	0.51
1.50	0.41	0.27	1.50	0.613	0.41
1.00	0.15	0.15	1.00	0.32	0.48
0.67	0.18	0.27	0.67	0.32	0.48
0.25	0.00	0.00	0.25	0.075	0.30
$\alpha_{\text{mean}} = 0.17$					0.41

The polymers had a higher content of II or III, respectively, than would correspond to the initial ratio. After prolonged polycondensation of AC with I and II, the I content in the polymer increased owing to exhaustion of the diamine mixture with respect to II, which had the principal share in the early reaction stage. The system of SC behaved similarly with III and IV. These results are explained by the different rates of diffusion of

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Heterochain polyamides...

S/062/62/000/011/012/021
B101/B144

the diamines into the organic phase. It is (in $M/cm^2 \cdot min$) $3.9 \cdot 10^{-7}$ for I, $6.07 \cdot 10^{-5}$ for II, and $1.07 \cdot 10^{-5}$ for III. The dissociation constants are $8.5 \cdot 10^{-5}$, $6.0 \cdot 10^{-10}$, and $5.1 \cdot 10^{-4}$, respectively. In the polymer, the content of radicals of the diamine primarily depends on the rate of diffusion. The reactivity is of secondary importance and has a compensating effect on the polymer composition if the slowly diffusing diamine has a higher reaction rate (dissociation constant). There are 3 figures and 5 tables.

ASSOCIATION: Institut elementoorganicheskikh soyedineniy Akademii nauk SSSR
(Institute of Elemental Organic Compounds of the Academy of Sciences USSR)

SUBMITTED: April 9, 1962

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32343
S/190/62/004/001/004/020
B101/B110

15.8150

AUTHORS: Korshak, V. V., Rogozhin, S. V., Volkov, V. I.

TITLE: Studies of coordination polymers. IX. Metal-containing polymers based on aliphatic dicarboxylic, α , α' -dihydroxydicarboxylic, and α , α' -dialkoxydicarboxylic acids

PERIODICAL: Vysokomolekulyarnyye soyedineniya, v. 4, no. 1, 1962, 20-24

TEXT: Synthesis and properties of polymers containing Zn, Cu, Cd, Co, or Ni on the basis of ω , ω' -hexadecanedicarboxylic acid (I), terephthalic acid (II), α , α' -dihydroxysebacic acid (III), and α , α' -dimethoxysebacic acid (IV) are described. III was synthesized from α , α' -dibromosebacic acid by saponification with 5% KOH solution, production of Cu salt with CuSO_4 , and formation of the free acid by precipitating Cu with H_2S . X

Dimethyl ester of IV was obtained from α , α' -dibromosebacic acid by sodium methyrate ($n_D^{20} = 1.4425$; boiling point = $128-130^\circ\text{C}/1-2$ mm Hg). Dipotassium salts of I, II, III, or IV were reacted with the chlorides or acetates of the

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B101/B110

Studies of coordination ...

metals in an aqueous or aqueous-alcoholic medium. Linear structure is assumed due to the thermal behavior and insolubility of the powdery precipitates obtained. The following data are listed: (A) Polymers from I, structure $\left[\begin{array}{c} \text{O} \\ | \\ -\text{C} \text{O} \text{M} \text{e} \text{O} \text{C} \text{O} \text{C} \text{H}_2 \\ | \\ \text{O} \end{array} \right]_n$; copper compound light blue, crystalline,

melting point 223 - 225°C (in capillary), maximum deformation (D_{\max}) at 201°C; Cd compound crystalline, white, melting point 211 - 213°C, $D_{\max} = 175^\circ\text{C}$; Zn compound crystalline, white, melting point 242 - 246°C, $D_{\max} = 221^\circ\text{C}$; (B) the Cu compound with II is light blue, crystalline, melting point 300°C (with decomposition), $D_{\max} = 335^\circ\text{C}$; (C) the composition of polymers of III differed with the conditions of synthesis. It is assumed that complexes with groups of adjacent chains or with molecules of the solvent are formed as a consequence of the incompletely occupied coordination sphere of the metal ion. Cd compound white, melting point 280-290°C (decomposition), $D_{\max} = 292^\circ\text{C}$; Zn compound white, melting

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Studies of coordination ...

point 330 - 350°C (decomposition), $D_{\max} = 327^{\circ}\text{C}$; Cu compound light blue.
melting point 330°C (decomposition), $D_{\max} = 341^{\circ}\text{C}$; Co compound red-violet,
melting point 250°C, $D_{\max} = 351^{\circ}\text{C}$; Zn compound white, melting point
280°C, $D_{\max} = 327^{\circ}\text{C}$; Ni compound green, melting point 300°C (decomposi-
tion), $D_{\max} = 365^{\circ}\text{C}$; (D) the Co compound with IV is light violet,
melting point 300°C (decomposition), $D_{\max} = 243^{\circ}\text{C}$; Zn compound light
yellow, melting point 140 - 220°C, $D_{\max} = 157^{\circ}\text{C}$. The low stability of
the compound with IV is explained by the fact that substitution of CH_3
for the hydrogen of hydroxyl groups prevents the formation of H bonds.
X-ray patterns of Zn polymers showed a decreasing crystallinity in the
series I > III > IV (the latter polymer being amorphous). There are 2
figures, 2 tables, and 4 references: 1 Soviet and 3 non-Soviet. The
two references to English-language publications read as follows: R.
Martin, H. Watermann, J. Chem. Soc., 2545, 1957; Ch. K. Ingold, J. Chem.

Card 3/4

Studies of coordination ...

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B101/B110

Soc., 119, 964, 1921.

ASSOCIATION: Institut elementoorganicheskikh soyedineniy AN SSSR
(Institute of Elemental Organic Compounds AS USSR)

SUBMITTED: January 18, 1961

Card 4/4

15 8110

32317
S/190/62/004/001/009/020
B101/B110

AUTHORS: Korshak, V. V., Gribova, I. A., Andreyeva, M. A., Popova, G. M.

TITLE: Polymers containing phosphorus. XXVII. Heterochained polyesters of vinyl phosphinic acid with some dihydroxy compounds

PERIODICAL: Vysokomolekulyarnyye soyedineniya, v. 4, no. 1, 1962, 58-63

TEXT: The authors report on the properties of esters of diethylene glycol (I) and 4,4'-dihydroxy-2,2-diphenyl propane (II) with mixtures of vinyl and methyl phosphinic acids. The syntheses of these esters have already been described (Vysokomolek. soyed., 2, 427, 1960; Izv. AN SSSR, Otd. khim. n., 1958, 880). Esters with I are colorless, viscous liquids. Their freezing point drops from -39°C (100% CH_3POCl_2) to -51°C with 100%

$\text{CH}_2=\text{CHPOCl}_2$ in the initial mixture. Esters with II are transparent, brittle solids soluble in dichloro ethane, chloroform, and tricresol, insoluble in ether, benzene, and dioxane. Their softening points drop from $55-56^{\circ}\text{C}$ to

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Polymers containing phosphorus. ...

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41-42°C (= 100% vinyl phosphinic acid) as the content of vinyl phosphinic acid increases. Structurization of the ester of I (in sealed ampuls, N₂ atmosphere, at 60°C for 15 hrs, or in an open test tube and in C₂H₄Cl₂ solution) by benzoyl peroxide, tert-butyl peroxide, azoisobutyric dinitrile, tert-butyl hydroperoxide, or cumene hydroperoxide, only occurred with a vinyl phosphinic acid content \geq 40% (gelatinous substances, softening points: 150-200°C the latter value with 100% CH₂=CHPO-). Esters with II could not be structurized under the experimental conditions, applied. There are 2 figures, 4 tables, and 4 Soviet references. X

ASSOCIATION: Institut elementoorganicheskikh soyedineniye AN SSSR
(Institute of Elemental Organic Compounds AS USSR)

SUBMITTED: January 28, 1961

Card 2/2

33375

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B110/B101

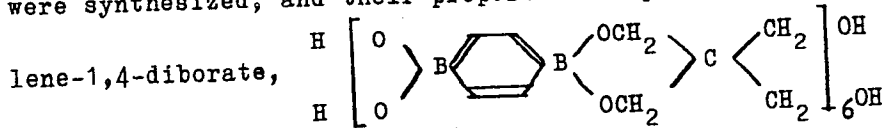
15.8150

AUTHORS: Korshak, V. V., Zamyatina, V. A., Ma Jui-jan, Oganessian, R.M.

TITLE: Polyesters and polymeric salts of boric and 1,4-phenylene diboric acids

PERIODICAL: Vysokomolekulyarnyye soyedineniya, v. 4, no. 2, 1962, 188-191

TEXT: V. A. Zamyatina and N. I. Bekasova (Usp. khimii, 30, 48, 1961) described the synthesis of highly thermostable polyesters of boric and substituted boric acids. In the present study, the polyesters of boric acid and 1,4-phenylene diboric acid (I) with pentaerythrite (II), the Zn- and Sn-organic salts of pentaerythrite hydroxydiboric acid (III) and I were synthesized, and their properties compared. Polypentaerythrite pheny-



is unmeltable and resistant to heat and hydrolysis. For producing a linear
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B110/B101

Polyesters and polymeric salts...

polyester, boric acid was condensed with pentaerythrite equimolecularly for 10 hr at 150 - 180°C in N₂ flow. The polymeric salts of III had linear structure. The molecular weight of insoluble polymers hydrolyzing in aqueous alkali could not be determined. The Zn salt of III contains more organic and fewer mineral fractions than had been calculated. Polycondensation of I with II yielded a polyester of calculated composition which was, however, not linear and insoluble. Anhydride was formed during the synthesis of polymeric salt of I from metal acetates, and some tributyl borate was separated out during that of Zn salt. Polyesters and salts resemble each other in mechanical and thermomechanical respect, and in outer appearance. The brittle white polyesters melt at >300°C. The polyester of I does not hydrolyze in the cold, that of boric acid does. The yellow brittle Sn-organic salts hydrolyze in the cold, and have low softening temperatures. The white Zn salts are friable, hydrolyze well, and melt at >500°C. There are 1 figure, 2 tables, and 2 references: 1 Soviet and 1 non-Soviet. The reference to the English-language publication reads as follows: W. R. Bamford, S. Fordham. High Temperature Resistance and Thermal Degradation of Polymers, Symposium, Sept. 1960, London, p. 127.

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B110/B101

Polyesters and polymeric salts...

ASSOCIATION: Institut elementoorganicheskikh soyedineniy AN SSSR
(Institute of Elemental Organic Compounds AS USSR)

SUBMITTED: February 2, 1961

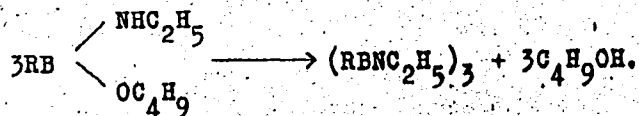
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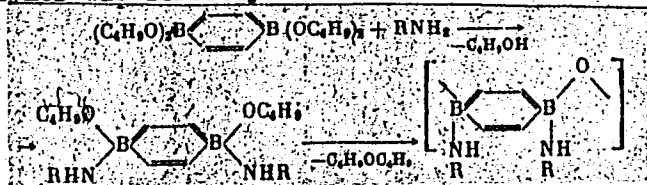
33376

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B110/B101

Polyamino polyanhydrides...



The reaction of tetra-n-butyl (or ethyl) ester of 1,4-phenylene diboric acid with aromatic (toluidine) and aliphatic (octylamine, hexamethylene diamine) amines and diamines for producing polymers with the B-N bond was studied. The organoboron polymer was directly formed:



the diamino diester of 1,4-phenylene diboric acid was converted to a polyamino anhydride under the test conditions. Interaction of two alkoxy groups with formation of an anhydride bond proceeds more readily than that of one alkoxy with one amino group or that of two amino groups. A minimum of 300°C is required for the latter reaction. All polymers are stable and high-melting.

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Polyamino polyanhydrides...

melting (m. > 300°C), those from monoamines are linear, those from diamines are steric and insoluble, and hydrolyze in boiling water. During polycondensation of tetraethoxy-1,4-phenylene diborate with anhydrous hydrazine, NH₃, and a volatile boron compound are probably separated. There are 1 figure, 1 table, and 3 references: 2 Soviet and 1 non-Soviet. The reference to the English-language publication reads as follows: D. R. Nielsen, W. E. McEwen, J. Amer. Chem. Soc., 79, 3081, 1957.

ASSOCIATION: Institut elementoorganicheskikh soyedineniy AN SSSR
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SUBMITTED: February 2, 1961

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34981
S/190/62/004/003/001/023
B110/B144

15.8/30
AUTHORS: Polyakova, A. M., Korshak, V. V., Lipatnikov, N. A.
TITLE: Polymerization of heterocyclic isopropenyl compounds.
II. 2-isopropenyl furan
PERIODICAL: Vysokomolekulyarnyye soyedineniya, v. 4, no. 3, 1962, 334-338

TEXT: The polymerization of 2-isopropenyl furan (I) was investigated by using (a) pressure without initiators, and (b) atmospheric pressure in the presence of ion catalysts. A viscous mass formed at 120°C and 6000 atm, which, after reprecipitation resulted in a powdery polymer; yield of 16.3 % (molecular weight 2230; polymerization coefficient 21). A temperature increase to 160°C reduced the molecular weight by half. Within a few minutes, I, in the presence of 2.56 mole% of $TiCl_4$ in methylene chloride at -72°C, forms a polymer of viscosity 0.09, yield of 46.6 %. In the presence of 5.12 mole% of $TiCl_4$ it forms a mixture of insoluble (80 %) and soluble polymer. In the presence of $Al(C_2H_5)_3/TiCl_4$, 11 % of insoluble polymer is formed. I polymerizes more readily than
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APPROVED FOR RELEASE: 06/14/2000

CIA-RDP86-00513R000824930004

Polymerization of heterocyclic...

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isopropenyl thiophene in the presence of ion catalysts in analogy to the behavior of corresponding vinyl compounds. Comparison of the monomer IR absorption spectra with that of polymer shows that the double bond of the isopropenyl group is ruptured and the furan ring conserved, the double bonds of which presumably participate in forming the insoluble polymer in ionic polymerization. It was found by X-ray analysis that the insoluble polymer obtained in the presence of $TiCl_4$ was poorly ordered, while the soluble polymer was almost amorphous. The thermomechanical curves of benzene-soluble polymers obtained from (a) and from (b) with 2.56 mole% of $TiCl_4$ were almost identical, but differed substantially from those of the polymers obtained with 5.12 mole% of $TiCl_4$. The insoluble fraction of these polymers shows no flow, and carbonizes at ~400°C. S. R. Rafikov is mentioned. Thanks are due to A. I. Kitaygorodskiy and co-workers, as well as to N. A. Chumayevskiy, for X-ray and spectroscopic investigations. There are 4 figures, 1 table, and 8 references: 5 Soviet and 3 non-Soviet. The three references to English-language publications read as follows: G. B. Bachman et al.: Industr. and

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34982
S/190/62/004/003/002/023
B110/B144

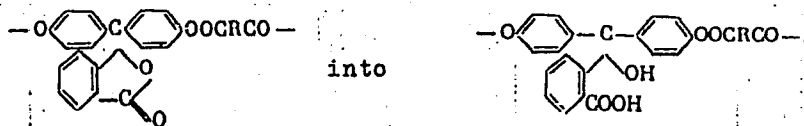
15.8110

AUTHORS: Korshak, V. V., Vinogradova, S. V., Salazkin, S. N.

TITLE: Heterochain polyesters. XXXIII. Polyarylates on phenolphthalein base

PERIODICAL: Vysokomolekulyarnyye soyedineniya, v. 4, no. 3, 1962, 339-344

TEXT: Homogeneous and mixed polyarylates (I) on phenolphthalein base were synthesized, and the effect of the initial compound structure on their properties was examined. The authors hoped to obtain a polymer which would be well soluble by virtue of the large phenolphthalein side groups and which would have a sufficiently high softening temperature owing to the polar group in the side group. The lactone group was to be modified to reactive carboxyl and hydroxyl groups as follows:

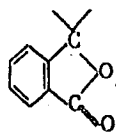
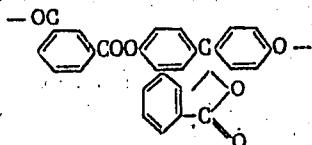


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Heterochain polyesters...

The properties of I are dependent on the structure of the initial components. I of terephthalic acid show the highest softening temperatures, followed by I of isophthalic, adipic, and sebacic acid. Substituting "dian" or resorcin for half the phenolphthalein in I lowers the softening temperature. A softening temperature rise is probably due to the increase of chain interaction caused by the polar groups:



The decrease in packing density raises the solubility of I on phenolphthalein base as compared with I on "dian" base. I on phenolphthalein base and isophthalic acid base dissolves in methylene chloride, chloroform, tetrachloro ethane, tetrahydrofuran, cyclohexanone. The partial substitution of phenolphthalein for bivalent phenols raises solubility. Films obtained from 5 % solutions of I with phenolphthalein and terephthalic acid retain

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Heterochain polyesters...

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> 50 % of their strength at 180°C. Amorphous structure of most of I on phenolphthalein base was established by X-ray structural analysis. Thanks are due to the teams of laboratoriya fiziki polimerov (Laboratory of Polymer Physics) and laboratoriya rentgenostrukturnogo analiza (Laboratory of X-ray Structural Analysis) for thermodynamic and X-ray analyses. There are 3 tables and 17 references: 13 Soviet and 4 non-Soviet. The two references to English-language publications read as follows: A. Conix, Industr. and Engng. Chem., 51, 147, 1959; W. M. Eareckson, J. Polymer Sci., 40, 399, 1959.

ASSOCIATION: Institut elementoorganicheskikh soyedineniy AN SSSR
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SUBMITTED: April 24, 1961

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34983
S/190/62/004/003/003/023
B110/B144

15.8110

AUTHORS: Korshak, V. V., Vinogradova, S. V., Iskenderov, M. A.

TITLE: Heterochain polyesters. XXXIV. Polyesters of aromatic dioxo condensed-ring compounds

PERIODICAL: Vysokomolekulyarnyye soyedineniya, v. 4, no. 3, 1962, 345-350

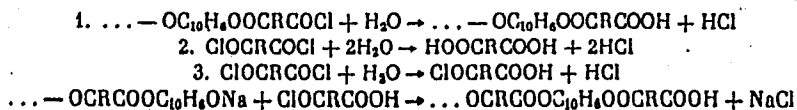
TEXT: Polyarylates were obtained on the base of isomeric diols of the naphthalene, anthracene, and phenanthrene series using interface poly-concentration. The effect of the feeding rate of initial compound solutions, of their concentration and ratio, and of the reaction temperature on yield and molecular weight of polyarylates of 1,6-dioxo naphthalene (I) and dicarboxylic acids (adipic (II), sebacic, and isophthalic (III) acid) was investigated. Best results were achieved by the addition of acid chloride solution to an aqueous alkali solution of I for 11-14 min. The highest polymer yield and viscosity were obtained at 0.10 N concentration of the initial solutions. 20°C was ideal for the interface condensation of 1,6-dioxo naphthalene with II, III, and sebacic acid. If one of the phases is aqueous, various competing reactions may, in polyesterification,

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Heterochain polyesters...

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take place at the interface. Some of them produce a polyester, while others prevent it from forming as, e.g., chain rupture due to hydrolysis of the acid chloride groups and of the initial dicarboxylic acid chloride:



The decrease in viscosity and yield of the polyarylates of I with an increase of the reaction temperature from 20 to 40°C is effected by the increase of the rate of these reactions in the polycondensation process at higher temperatures, while the decrease in viscosity and yield at low temperatures is effected by a drop in the rate of the polymer-forming reaction. Yield and viscosity of polyarylates depend on the different hydrolyzing capacities of the acid chlorides. A 0.2-mole excess of dicarboxylic acid chloride, required as compensation for the acid chloride lost through hydrolysis, provided maximum viscosity (0.22 in polyarylates of III, and 0.16 in those of II) and yield (84 % in III and 35 % in II). Excess of

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Heterochain polyesters...

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I or of acid chloride (> 0.2 mole) leads to chain rupture by the formation of phenolate or acid chloride groups at the chain terminals. The best NaOH amount is 0.1 mole excess in III and 0.2 mole excess in II. The amount of reactive phenolate of I drops with NaOH deficiency, as I does not react spontaneously. NaOH excess causes the initial acid chloride and the polymer chain to hydrolyze. There are 4 figures, 2 tables, and 16 references: 10 Soviet and 6 non-Soviet. The two references to English-language publications read as follows: A. Conix, Industr. and Engng. Chem., 51, 147, 1959; I. A. Ambler, I. T. Seanlan, Industr. and Engng. Chem., 19, 417, 1927.

ASSOCIATION: Institut elementoorganicheskikh soyedineniy AN SSSR
(Institute of Elemental Organic Compounds AS USSR)

SUBMITTED: February 9, 1961

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