"APPROVED FOR RELEASE: 04/03/2001 CIA-RDP86-00513R000100130002-4

83704
S/190/60/002/006/009/012
B015/B064

15.8101 also 2209

AUTHORS: Medvedev, S. S., Abkin, A. D., Khomikovskiy, P. M., Gerasimov, G. N., Gromov, V. F., Chikin, Yu. A., Tsingister, V. A., Auer, A. L., Yakovleva, M. K., Mezhirova, L. P., Matveyeva, A. V., Bezzubik, Z. G.

TITLE: Polymerization of Ethylene Under the Influence of γ-Radiation

PERIODICAL: Vysokomolekulyarnyye soyedineniya, 1960, Vol. 2, No. 6, pp. 904-915

TEXT: The radiation-chemical polymerization of ethylene in the gaseous phase and in organic substances was investigated at different pressure and radiation dose as well as some properties of the polymers formed. Co^{60} γ-radiation sources of the institut im. Karpova (Institute imeni Karpov) (1400, 1800, and 20000 gram equiv. Ra) and pressures of 50-300 atm, radiation dose of 17 to 165 r/sec, and 25°C (some experiments were made at 50°C) were the conditions. The experiments were carried out in a corresponding device (Fig. 1). The ethylene used was mass-

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ABKIN, A. D.

Investigation of copolymerization of hexadecyl and methyl acrylates in a toluene solution. S. N. Kamenskaya, A. D. Abkin, and S. S. Medvedev. *Doklady Akad. Nauk S.S.S.R.* 106, 855-8(1956); cf. *C.A.* 45, 3227e.—The relative reactivity of polymerization of 2 chemically similar monomers and their copolymerization was studied on the basis of the results reported before (*loc. cit.*). Me acrylate was purified by washing, drying, and distn. at 38-9° and 785 mm. Hg. Ether distd. from the monomer was used in its polymerization, doing away with the induction period. Hexadecyl acrylate was synthesized from hexadecanol and Me acrylate in the presence of *p*-toluenesulfonic acid. The ester was distd. *in vacuo* in the presence of metallic Cu, and the 155-60° fraction at 1.4 mm. Hg, m.p. 24°, n^{20} = 1.4509, d^{20} = 0.859, was collected. Pure Br_2O_2 was used as the reaction initiator. For copolymerization, a toluene soln. with the monomer concn. of 1.5 moles/l. was used. The polymerization rate was observed dilatometrically, at 50 ± 0.05°. The hexadecyl acrylate polymerization rate was found to be 2.3 times greater than of Me acrylate, and this rate was found to be the same at lower concns. of monomers. The copolymerization rate was calcd. by using the previously derived formula, which involved the use of the individual polymerization rates of the monomers, and the coeff. λ which characterizes the ratio of the ratio of the constants of the individual monomers polymerization initiation. The value of λ was found to be 6 from the kinetic data, and nearly the same value from the av. of polymerization. By assuming the value for the Me acrylate chain growth rate $K_{A-A} = 10^{8}e^{-2\pi\varrho/RT}$ (Matheson, *et al.*, *C.A.* 46, 1852e), the values for K_{A-A} = 1558; K_{B-B} = 1507, K_{A-B} = 1731; and K_{B-A} = 1256.

W. M. Sternberg

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M. A. YOUTZ

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Phys. Chem. Inst. im. Karpov

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"APPROVED FOR RELEASE: 04/03/2001 CIA-RDP86-00513R000100130002-4

MAMONTOVA, O.;: ABKIN, A.; MEDVEDEV, S.

Polymerization Processes Laboratory, Moscow Physico-Chemical Institute im. L. Ya. Karpov, (-1939-). "The Kinetics of Polymerization of Butadiene - 1.3 in the Presence of Potassium Phenylisopropyl (Fenilizopropilkaliya)".

Zhur. Fiz. Khim., Vol. 14, No. 1, 1940.

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"APPROVED FOR RELEASE: 04/03/2001 CIA-RDP86-00513R000100130002-4

Polymerization of Ethylene Under the Influence of γ-Radiation

spectroscopically analyzed by M. V. Tikhomirov and M. V. Gur'yev. The molecular weight of the polyethylene obtained was determined by the method of light scattering by I. G. Soboleva and N. V. Mekletsova; particular data on this will be given in a separate paper. The experiments of polymerization in heptane, cyclohexane, methanol, and acetone (50 atm, 25°C, ~100 r/sec) showed (Table 1) that reaction proceeds ten times more rapidly than in the gaseous phase. The polymers formed have a molecular weight of 20000-40000. Polymers of the structure $Cl_3C(C_2H_4)_2Cl$ (60%) and $Cl_3C(C_2H_4)_3Cl$ (20%) form in good yield in carbon tetrachloride. Polymerization in the gaseous phase was investigated at constant pressure (100-300 atm, 72 r/sec) and decreasing pressure (100 and 150 atm, 17-165 r/sec, 25° and 50°C). The polymer yield increases rapidly if experiments are made in the presence of polyethylene (Table 2). To begin with, the polymerization rate increases with time and reaches then a constant value. The mean molecular weight and the characteristic viscosity of the polymers increases with proceeding transformation (Table 3) The mean reaction rate amounts to 16.9 g/l.hour at 300 atm, 25°C, a duration of 24 hours and radiation dose of 72 r/sec, and the maximum rate

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Polymerization of Ethylene Under the Influence of γ-Radiation

20.5 g/l.hour (Table 4). The mean molecular weight and viscosity of polyethylene (Table 5) rise with pressure (i.e. the ethylene concentration). The maximum rate of polymerization increases somewhat with the radiation dose with a proportionality factor of 0.3, while the radiation-chemical yield decreases with an increase in the radiation dose with a factor of 0.7. The molecular weight of polyethylene increases with a reduction of the radiation dose with a factor of 0.7. The molecular weight of polyethylene increases with decreasing radiation dose (Table 6). A temperature increase from 25°C to 50°C at constant ethylene concentration (330 g/l) causes a lesser increase in the polymerization rate and the molecular weight (Table 7). Investigations carried out by Yu. M. Malinskiy and B. I. Evgrev in the laboratory of radiochemistry of the authors' institute showed that the polyethylene obtained has a higher density (0.945-0.975 g/cm^3) and degree of crystallization than high-pressure polyethylene, differs, however, only slightly from the latter with respect to the tensile strength. In conclusion, the authors thank A. Kh. Breger, V. B. Osipov, and V. A. Gol'din for assisting in carrying out the experiments with the gamma emitters. There are 8 figures, 7 tables, and 11 references: 5 Soviet, 4 US, 1 British, and 1 Belgian.

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Polymerization of Ethylene Under the Influence of γ -Radiation

S/190/60/002/006/009/012
B015/B064

ASSOCIATION: Fiziko-khimicheskiy institut im. L. Ya. Karpova
(Physico-chemical Institute imeni L. Ya. Karpov)

SUBMITTED: February 24, 1960

X

Card 4/4

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"APPROVED FOR RELEASE: 04/03/2001 CIA-RDP86-00513R000100130002-4

S/844/62/000/000/075/129
D423/D307

AUTHOR: Abkin, A. D.

TITLE: Radiation polymerization

SOURCE: Trudy II Vsesoyuznogo soveshchaniya po radiatsionnoy khimii. Ed. by L. S. Polak. Moscow, Izd-vo AN SSSR, 1962, 430-449

TEXT: Results of (mostly Western) investigations in the field of radiation polymerization are reviewed. The subjects covered include radical polymerization, polymerization in a variety of systems and also in the three phases. Ionic polymerization in the liquid phase is discussed for iso-butylene, styrene, butadiene and trimethyl-2,4,4-pentene-1. Some conclusions are drawn concerning the mechanisms of the polymerization processes and equations and graphs are presented to show the relations between the various parameters. Experiments were carried out over the range +60 to -112°C. Carbanionic polymerization is also considered, in some detail, for acrylonitrile in various solvents. It was shown that radiation polymeri-

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zation proceeded by an anionic mechanism, the rate of which in trimethylamine, over the range +25 to -112°C, fell initially to a minimum of about -50°C and then increased rapidly. Increase in the rate of polymerization was also accompanied by a significant increase in molecular weight of the polymer. Addition of styrene to solutions of acrylonitrile in dimethyl-formamide at -78°C reduced the rate of polymerization. A section is devoted to the mechanism of ionic polymerization in the liquid phase and a theory is established for the monomolecular mechanism of chain rupture in the low-temperature polymerization of iso-butylene and styrene, associated with ejection by the growing carbonium ion of a proton and the formation in the final group of the polymer chain of a double bond. An equation is given for the ratio of joint polymerization,

$$\omega = \frac{(\lambda + 1)(r_1 A^2 + 2AB + r_2 B^2)\omega_A \omega_B}{\lambda \omega_B r_1 A^2 + X\omega_A \omega_B AB + \omega_A r_2 B^2} \qquad (1)$$

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where A and B are the monomer concentrations; ω_A and ω_B are the individual rates of polymerization; λ is a quantity characterizing the ratio of the rates of formation of initial active centers from the monomers A and B by their joint polymerization; X is a quantity characterizing the ratio of the constants of the rates of 'cross' chain rupture and the rates of joint chain growth. There are 3 tables, 8 figures and 80 references.

ASSOCIATION: Fiziki-khimicheskiy institut im. L. Ya. Karpova (Physico-Chemical Institute im. L. Ya. Karpov)

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[redacted]

[redacted] AN SSSR [redacted]

[redacted] polymerization, copolymerization, radiat[redacted] polymerization, iso-

[redacted] ionic mechanism, [redacted]ion polymerizat-

tion constant, alkyl halide

ABSTRACT The role of solid admixtures in such reactions was explored in the separate and copolymerization of the title products under the influence of gamma rays (70 rad/sec., Co^{60}) at 0C, using as admixtures glass powder or ZnO in quantities corresponding in volume to the volume of the liquid phase. The kinetics of separate polymerization was studied with the dilatometer, copoly-

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L 15630-65
ACCESSION NR: AP4043843

[illegible] published

[illegible] weight obtained [illegible]

[illegible] resp

for isobutylene and styrene with [illegible] of the copolymeriza-
[illegible] The latter was always lower than [illegible]
[illegible] The probable reasons [illegible]

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ACCESSION NR: AP4043843

ionic radiation polymerization, probably related to the interaction of monomers with the protons forming in the chemi-adsorbed layer. Detailed data on the [illegible] has 4 figures.

ASSOCIATION: Fiziko-khimicheskiy institut im. L. Ya. Karpov (Physico-Chemical Institute)

SUBMITTED: 25Mar64 ENCL: 00

SUB CODE: GC NO REF SOV: [illegible]

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"APPROVED FOR RELEASE: 04/03/2001 CIA-RDP86-00513R000100130002-4

L 4289-66 EWT(m)/EPF(c)/EPF(n)-2/EWP(j)/T/EWA(h)/EWA(1) RPL WW/GG/RM

ACCESSION NR: AP5024006 UR/0020/65/164/002/0365/0367

AUTHOR: Gerasimov, G. N.; Sabirova, T. M.; Khomikovskiy, P. M.; Abkin, A. D.

TITLE: Radiation polymerization of vinyl chloride in solid solutions at low temperatures

SOURCE: AN SSSR. Doklady, v. 164, no. 2, 1965, 365-367

TOPIC TAGS: vinyl chloride, radiation polymerization, mineral oil, solid solution

ABSTRACT: The polymerization of vinyl chloride was carried out in mineral oil at a dose rate of 70 rad/sec (Co^{60}) and temperatures of -78 and -196C, i.e., above and below the melting point of vinyl chloride. Considerable postpolymerization was found to take place during thawing of the solutions, so that the latter was carried out very rapidly when kinetic data were taken. The kinetic curves obtained show that at -196C the reaction rate decreases sharply during the first stage, and the polymerization practically ceases at 15 - 20% conversion; the yield of polymer becomes markedly reduced when the vinyl chloride content increases from 6 to 15%. At -78C, the reaction rate increases sharply at first, then reaches a maximum, and declines rapidly at 50 - 60% conversion. The products formed are low-molecular polymers. It is postulated on the basis of the kinetic data that the polymerization of vinyl chloride in a solid mineral oil solution is determined by a

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definite ordered arrangement of vinyl chloride molecules. The structure of the frozen systems also affects the polymerization process. In contrast to amorphous solutions of vinyl chloride in low-molecular paraffins, the solid system vinyl chloride-mineral oil is a microheterogeneous one; in the presence of microheterogeneity, significant kinetic effects can take place. Orig. art. has: 2 figures.

ASSOCIATION: Fiziko-khimicheskiy institut im. L. Ya. Karpova (Physiochemical Institute)

SUBMITTED: 10Dec64 ENCL: 00 SUB CODE: MT GC

NO REF SOV: 001 OTHER: 005

Card 2/2

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"APPROVED FOR RELEASE: 04/03/2001 CIA-RDP86-00513R000100130002-4

L 26138-66 EWT(m)/EPF(n)-2/EWP(j)/T/EWA(h)/EWA(l) IJP(c) WW/GG/RM

ACC NR: AP6015061 (A) SOURCE CODE: UR/0190/66/008/005/0961/0962

AUTHOR: Bruk, M. A.; Gromov, V. F.; Chernyak, I. V.; Khomikovskiy, P. M.; Abkin, A. D.

ORG: None

TITLE: Radiation-induced polymerization of tetrafluoroethylene and acrylonitrile at 4.2 K

SOURCE: Vysokomolekulyarnyye soyedineniya, v. 8, no. 5, 1966, 961-962

TOPIC TAGS: tetrafluorothylene, acrylonitrile, bulk polymerization, low temperature polymerization

ABSTRACT: Polymers of tetrafluoroethylene or acrylonitrile have been prepared by bulk radiation-induced polymerization of the monomers at 4.2 K. Molten monomer samples were frozen at a given rate in liquid nitrogen, placed in a cryostat with liquid helium, and irradiated. Defrosting of the samples was conducted under conditions which excluded post-polymerization. The authors assume that in the course of polymerization of the monomers at low temperatures the bulk temperature of the samples does not determine the character of the polymer chain formation, which takes place in "hot" regions. The polymer chains grow before relaxation of the vibration excitation of molecules in "hot" regions has time to occur. The authors also assume that polymerization follows the cooperative mechanism which does not require activation for the addition of individual monomer molecules. Orig. art. has: 1 figure. [BO]

SUB CODE: 07, 11/ SUBM DATE: 06Jan66/ ORIG REF: 003/ OTH REF: 001/ ATD PRESS: 4251

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"APPROVED FOR RELEASE: 04/03/2001 CIA-RDP86-00513R000100130002-4

ACCESSION NR: AP4012181 S/0191/64/000/002/0003/0006

AURHORS: Abkin, A. D.; Auer, A. L.; Breger, A. Kh.; Vaynshteyn, B. I.; Voropayev, Yu. V.; Gol'din, V. A.; Gromov, V. F.; Osipov, V. B.; Sy*rkus, N. P.; Ushakov, V. D.; Khomikovskiy, P. M.; Tsingister, V. A.; Chikin, Yu. A.

TITLE: Radiation polymerization of ethylene in enlarged laboratory apparatus.

SOURCE: Plasticheskiye massy*, no. 2, 1964, 3-6

TOPIC TAGS: ethylene, radiation polymerization, reactor design, reactor surface area, reaction rate, polymer yield, reactor temperature field

ABSTRACT: Radiation polymerization of ethylene was conducted in laboratory reactors of 1-2 liter capacity (fig. 1 & 2). Based on tolerances admitted in this work, it was found that the temperature field can be calculated with sufficient accuracy. Comparison of reaction rates and yield of ethylene polymer shows that these factors are independent of the specific surface of the reaction space. Thus

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ACCESSION NR: AP4012181

commercial scale apparatus can be designed by estimating the process rate and yield dependence on pressure, temperature and dosage rate without concern for specific surface area of the reactor. Orig. art. has: 1 Table and 5 Figures

ASSOCIATION: None

SUBMITTED: 00 DATE ACQ: 26Feb64 ENCL: 02

SUB CODE: MA NR REF SOV: 005 OTHER: 003

Card 2/4

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"APPROVED FOR RELEASE: 04/03/2001 CIA-RDP86-00513R000100130002-4

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B101/B215

15,8115

AUTHORS: Gantmakher, A. R., Medvedev, S. S., Abkin, A. D.

TITLE: Low-temperature polymerization of ethylene tetrafluoride in liquid phase by the action of gamma radiation

PERIODICAL: Vysokomolekulyarnyye soyedineniya, v. 3, no. 2, 1961, 320

TEXT: In this letter to the editor the authors state that they were the first to examine the liquid phase polymerization of ethylene tetrafluoride under the action of gamma radiation. The polymerization was conducted in sealed glass phials in the absence of oxygen, at -55°C and 10 roentgen/sec. Under these conditions, the reaction took place at a high rate and was accompanied by the formation of a solid polymer. Afer one hour, the yield of polyethylene tetrafluoride was 35%. It was increased up to 95% by a radiation of 6 hr. The studies were continued by Ye. F. Volkova, A. V. Fokin, V. M. Belikov (Tezisy dokladov na II Vsesoyuznom soveshchanii po radiatsionnoy khimii, 1960 str. 65 (Theses of the Reports on the 2nd All-Union Conference of Radiation Chemistry, Moscow, 1960, p. 65) Ref. 1). The

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Low-temperature polymerization of ....

publications show (S. S. Medvedev, A. D. Abkin, P. M. Khomikovskiy, G. N. Gerasimov, V. F. Gromov et al., Vysokomolek. soyed. 2, 904, 1960, Ref. 2) that ethylene under similar conditions is polymerized more slowly. This difference in the polymerization rates of ethylene tetrafluoride and ethylene may be due to a slower rupture of chains by recombination in the polymerization of ethylene tetrafluoride due to repulsive forces. The latter occur in the approximation of perfluorinated radicals of polyethylene tetrafluoride. The slow rate of chain ruptures may also be due to topochemical peculiarities occurring in the polymerization of ethylene tetrafluoride. [Abstracter's note: this is a full translation from the original.] There are 2 Soviet-bloc references.

SUBMITTED: October 29, 1960

Card 2/2

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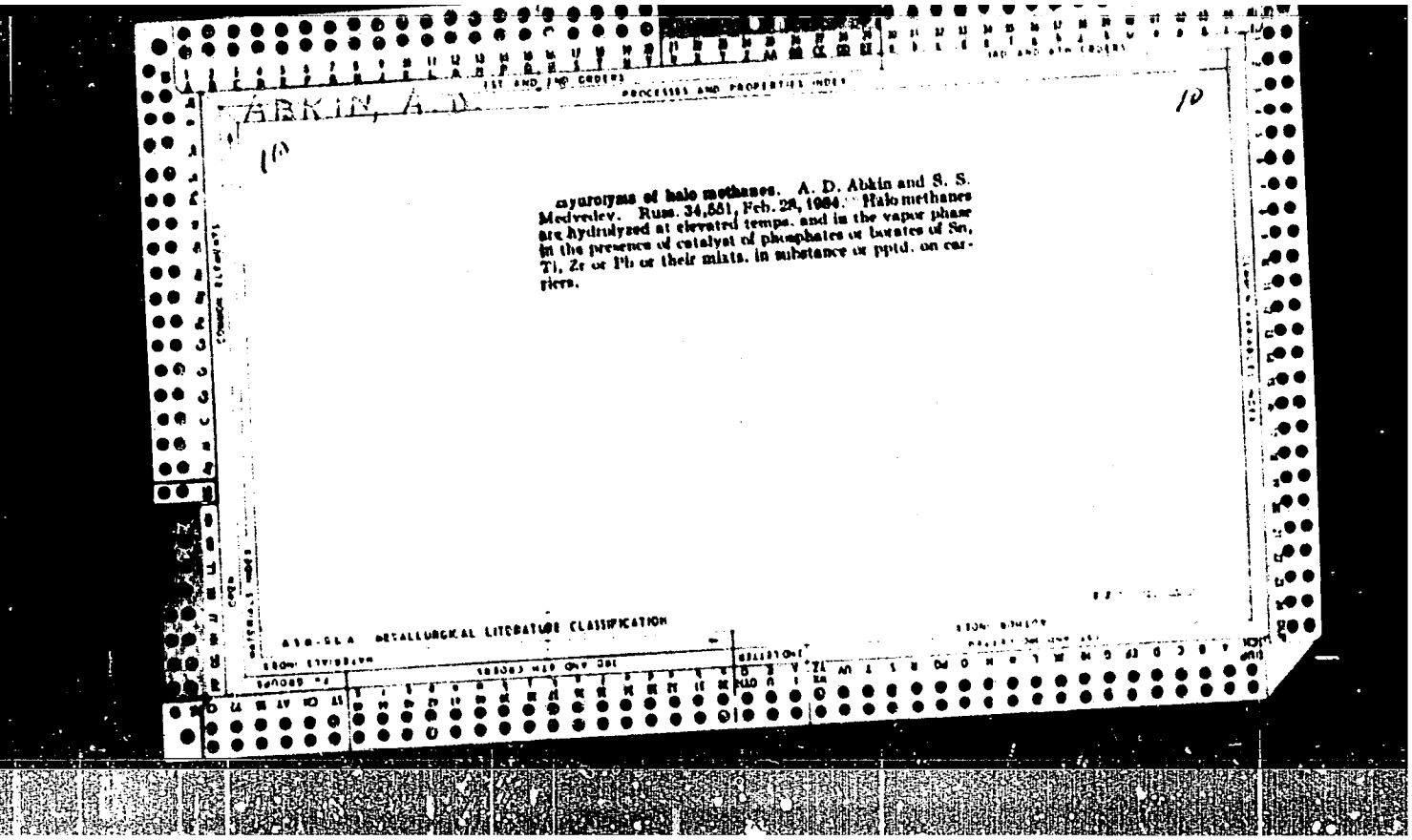

ABKIN, A. D.

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Hydrolysis of halo methanes. A. D. Abkin and S. S. Medvedev. Russ. 34,551, Feb. 28, 1984. Halo methanes are hydrolyzed at elevated temps. and in the vapor phase in the presence of catalyst of phosphates or borates of Sn, Ti, Zr or Pb or their mixts. in substance or pptd. on carriers.

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION

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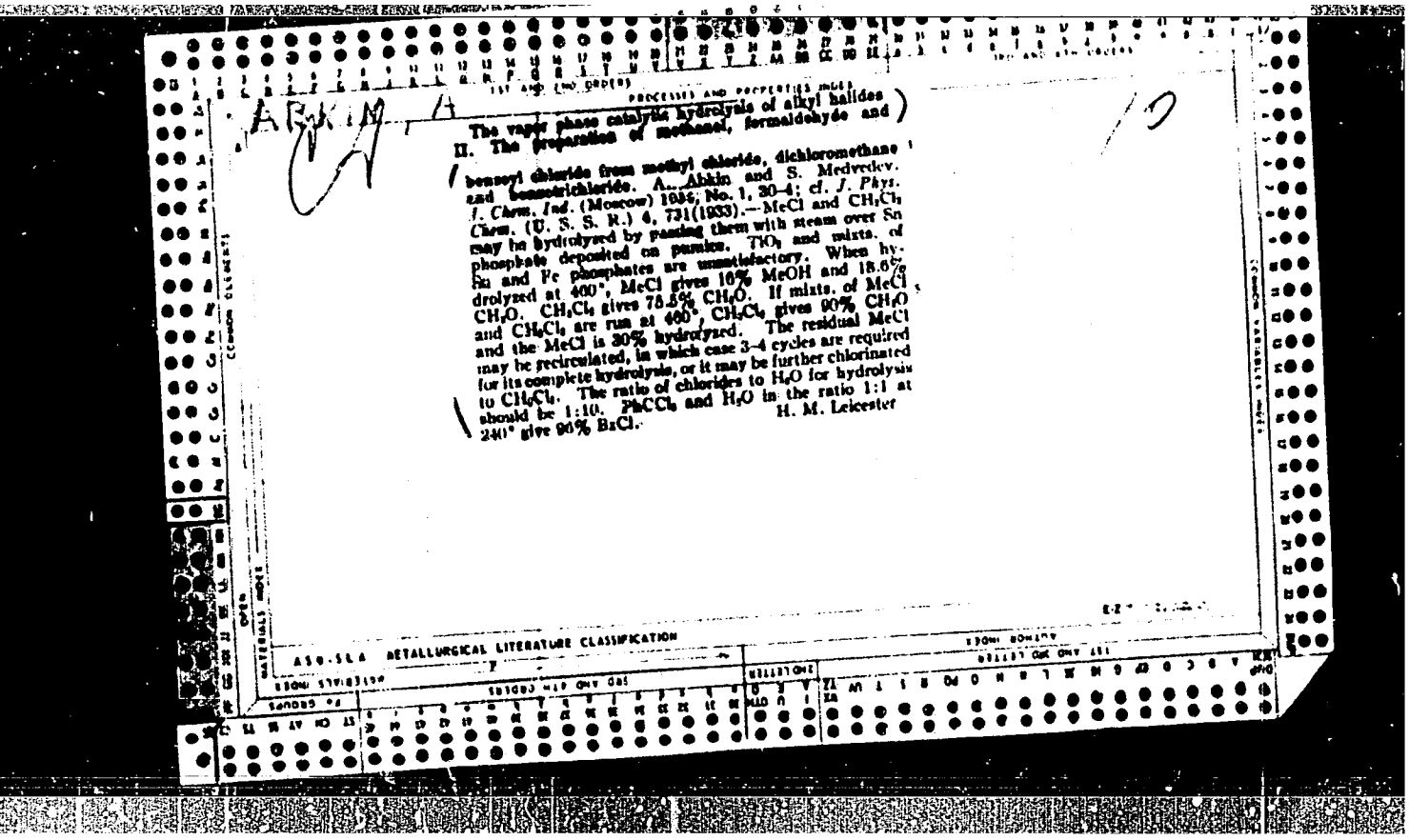

The vapor phase catalytic hydrolysis of alkyl halides
II. The preparation of methanol, formaldehyde and benzoyl chloride from methyl chloride, dichloromethane and benzotrichloride. A. Abkin and S. Medvedev. *J. Chem. Ind.* (Moscow) 1936, No. 1, 30–4; cf. *J. Phys. Chem.* (U. S. S. R.) 4, 731(1933).—MeCl and CH_2Cl_2 may be hydrolyzed by passing them with steam over Sn phosphate deposited on pumice. TiO_2 and mixts. of Sn and Fe phosphates are unsatisfactory. When hydrolyzed at 400°, MeCl gives 10% MeOH and 18.6% CH_2O. CH_2Cl_2 gives 75.5% CH_2O. If mixts. of MeCl and CH_2Cl_2 are run at 460°, CH_2Cl_2 gives 90% CH_2O and the MeCl is 30% hydrolyzed. The residual MeCl may be recirculated, in which case 3–4 cycles are required for its complete hydrolysis, or it may be further chlorinated to CH_2Cl_2. The ratio of chlorides to H_2O for hydrolysis should be 1:10. $PhCCl_3$ and H_2O in the ratio 1:1 at 240° give 90% BzCl.

H. M. Leicester

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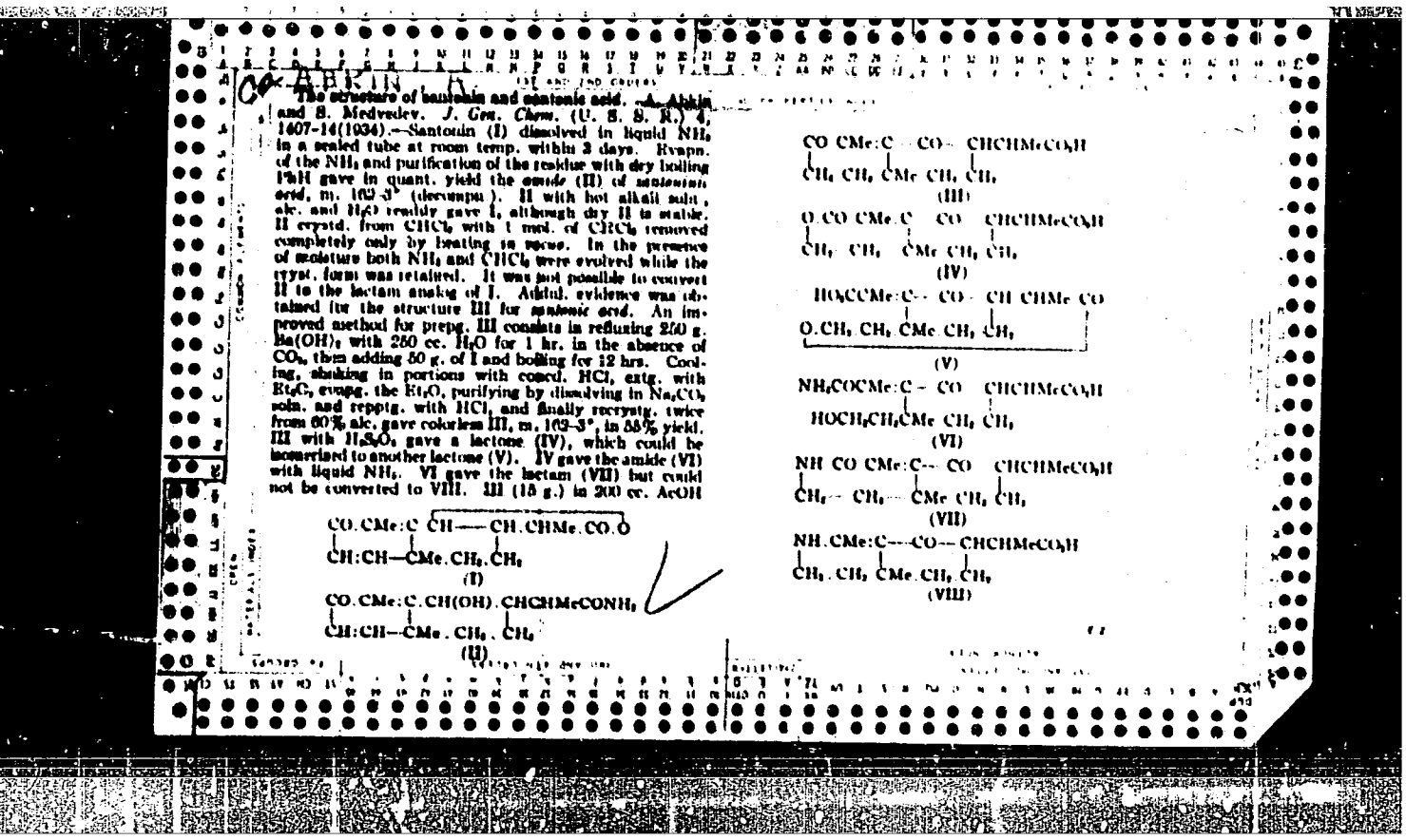


ABKIN A.

The structure of santonin and santonic acid. —A. Abkin and S. Medvedev. *J. Gen. Chem.* (U. S. S. R.) 4, 1607-14(1934).—Santonin (I) dissolved in liquid NH_3 in a sealed tube at room temp. within 3 days. Evapn. of the NH_3 and purification of the residue with dry boiling Et_2O gave in quant. yield the *amide* (II) of *santonian acid*, m. 162-3° (decompn.). II with hot alkali soln., alc. and H_2O readily gave I, although dry II is stable. II crystd. from $CHCl_3$ with 1 mol. of $CHCl_3$ removed completely only by heating in vacuo. In the presence of moisture both NH_3 and $CHCl_3$ were evolved while the cryst. form was retained. It was not possible to convert II to the lactam analog of I. Addtl. evidence was obtained for the structure III for *santonic acid*. An improved method for prepg. III consists in refluxing 250 g. $Ba(OH)_2$ with 250 cc. H_2O for 1 hr. in the absence of CO_2, then adding 50 g. of I and boiling for 12 hrs. Cooling, shaking in portions with concd. HCl, extg. with Et_2O, evapg. the Et_2O, purifying by dissolving in Na_2CO_3 soln. and repptg. with HCl, and finally recrystg. twice from 60% alc. gave colorless III, m. 162-3°, in 55% yield. III with H_2SO_4 gave a lactone (IV), which could be isomerized to another lactone (V). IV gave the amide (VI) with liquid NH_3. VI gave the lactam (VII) but could not be converted to VIII. III (15 g.) in 200 cc. AcOH

(I)

(II)

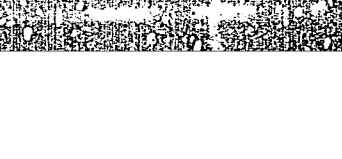
(III)

(IV)

(V)

(VI)

(VII)



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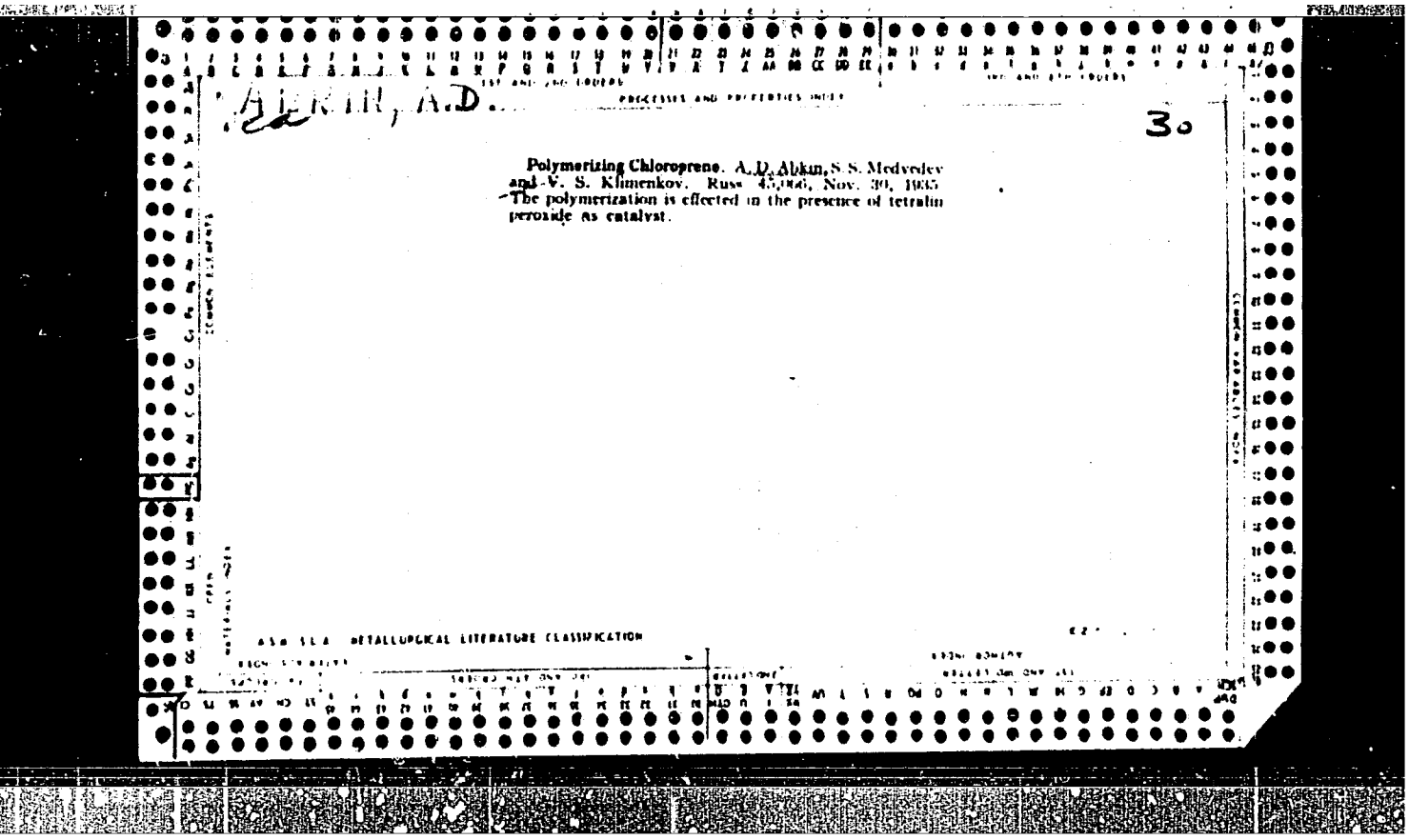

ALKIN, A.D.

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Polymerizing Chloroprene. A. D. Alkin, S. S. Medvedev and V. S. Klimenkov. Russ 45,966, Nov. 30, 1935. The polymerization is effected in the presence of tetralin peroxide as catalyst.

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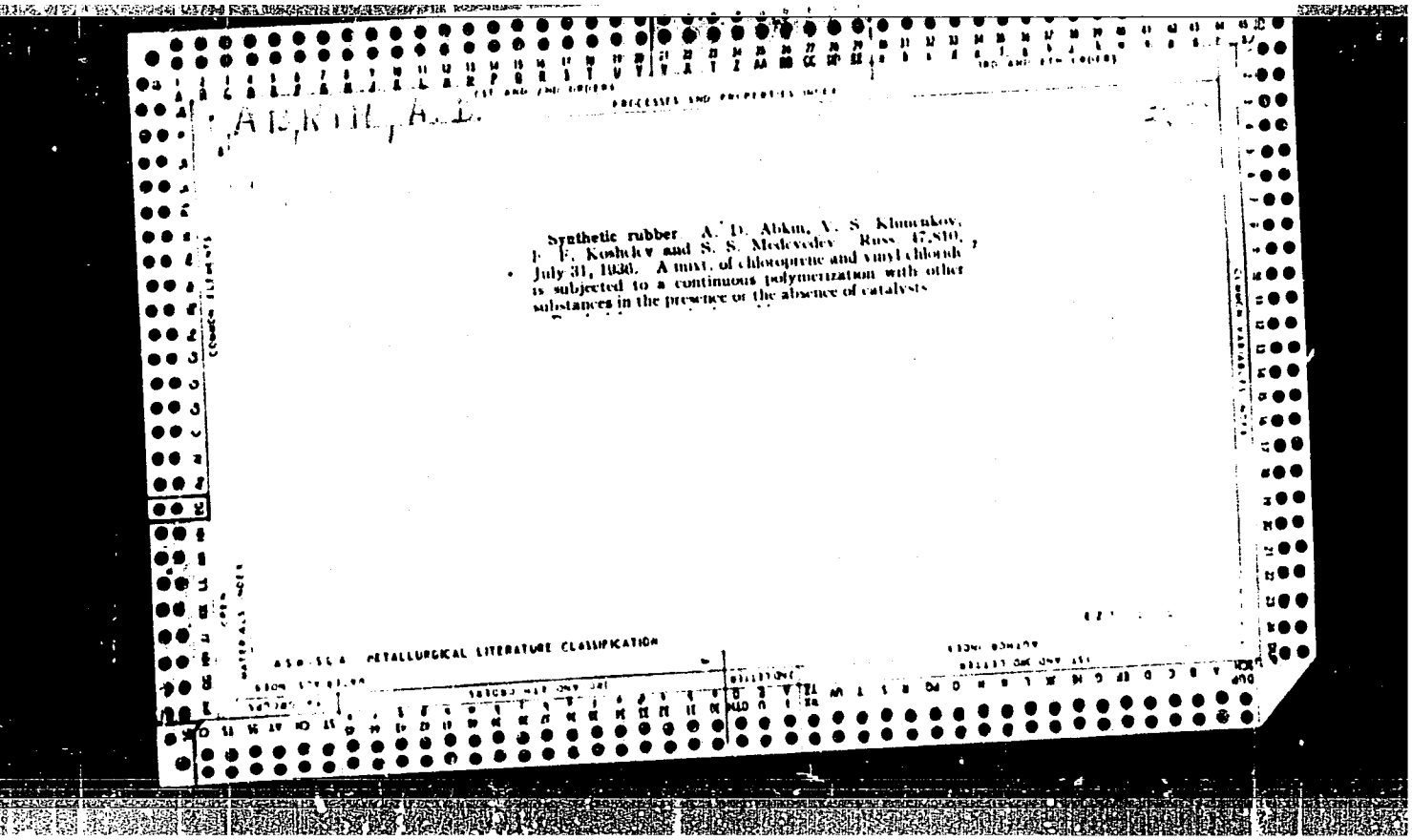

ABKIL, A.D.

Synthetic rubber. A. D. Abkin, V. S. Khmurakov, P. F. Koshelev and S. S. Medvedev. Russ. 47,810, July 31, 1936. A mixt. of chloroprene and vinyl chloride is subjected to a continuous polymerization with other substances in the presence or the absence of catalysts.

ASTIA METALLURGICAL LITERATURE CLASSIFICATION

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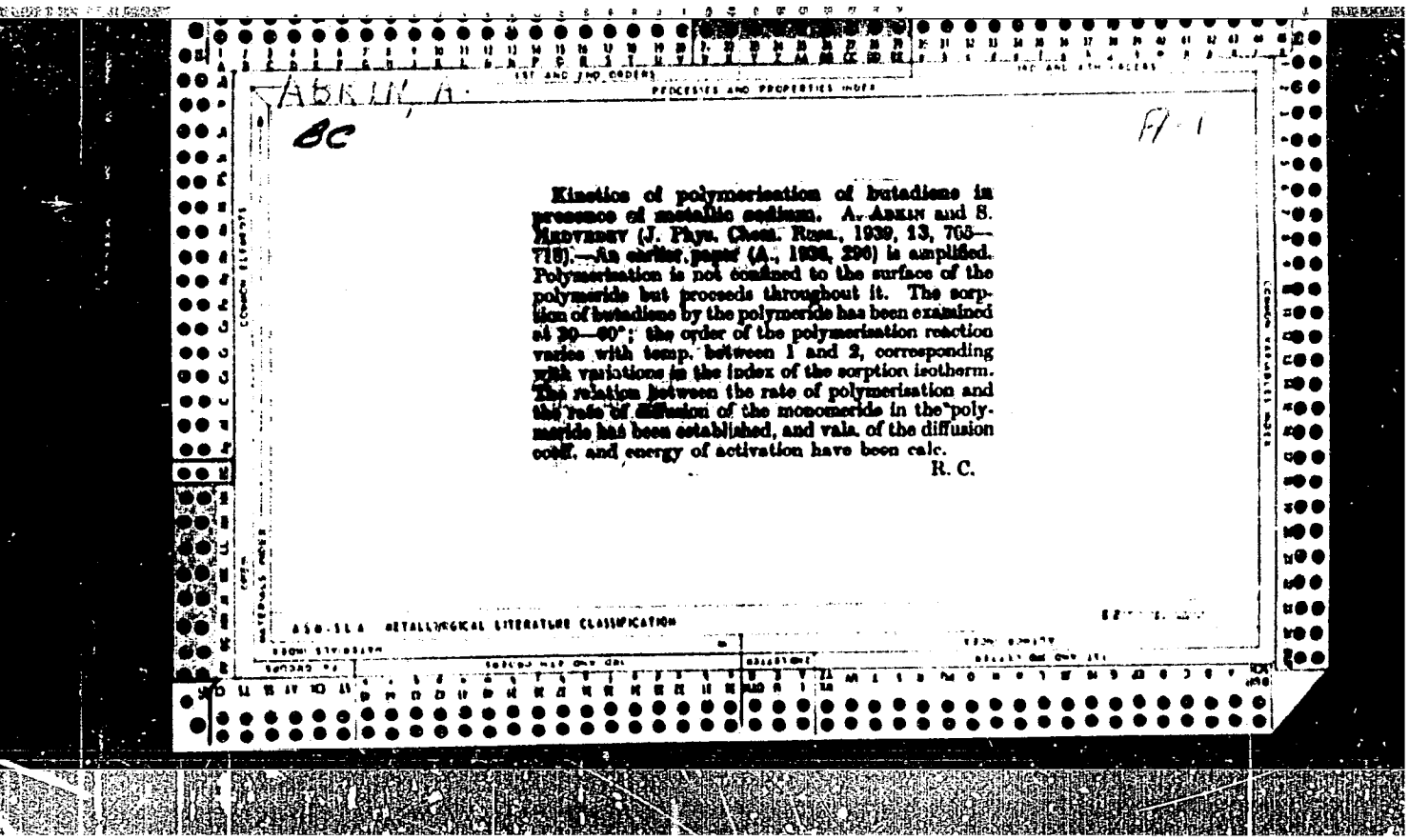

ABKIN, A.

BC

A-1

Kinetics of polymerisation of butadiene in presence of metallic sodium. A. ABKIN and S. MEDVEDEV (J. Phys. Chem. Russ., 1939, 13, 765—718).—An earlier paper (A., 1936, 296) is amplified. Polymerisation is not confined to the surface of the polymeride but proceeds throughout it. The sorption of butadiene by the polymeride has been examined at 30—60°; the order of the polymerisation reaction varies with temp. between 1 and 2, corresponding with variations in the index of the sorption isotherm. The relation between the rate of polymerisation and the rate of diffusion of the monomeride in the polymeride has been established, and vals. of the diffusion coeff. and energy of activation have been calc.

R. C.

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION

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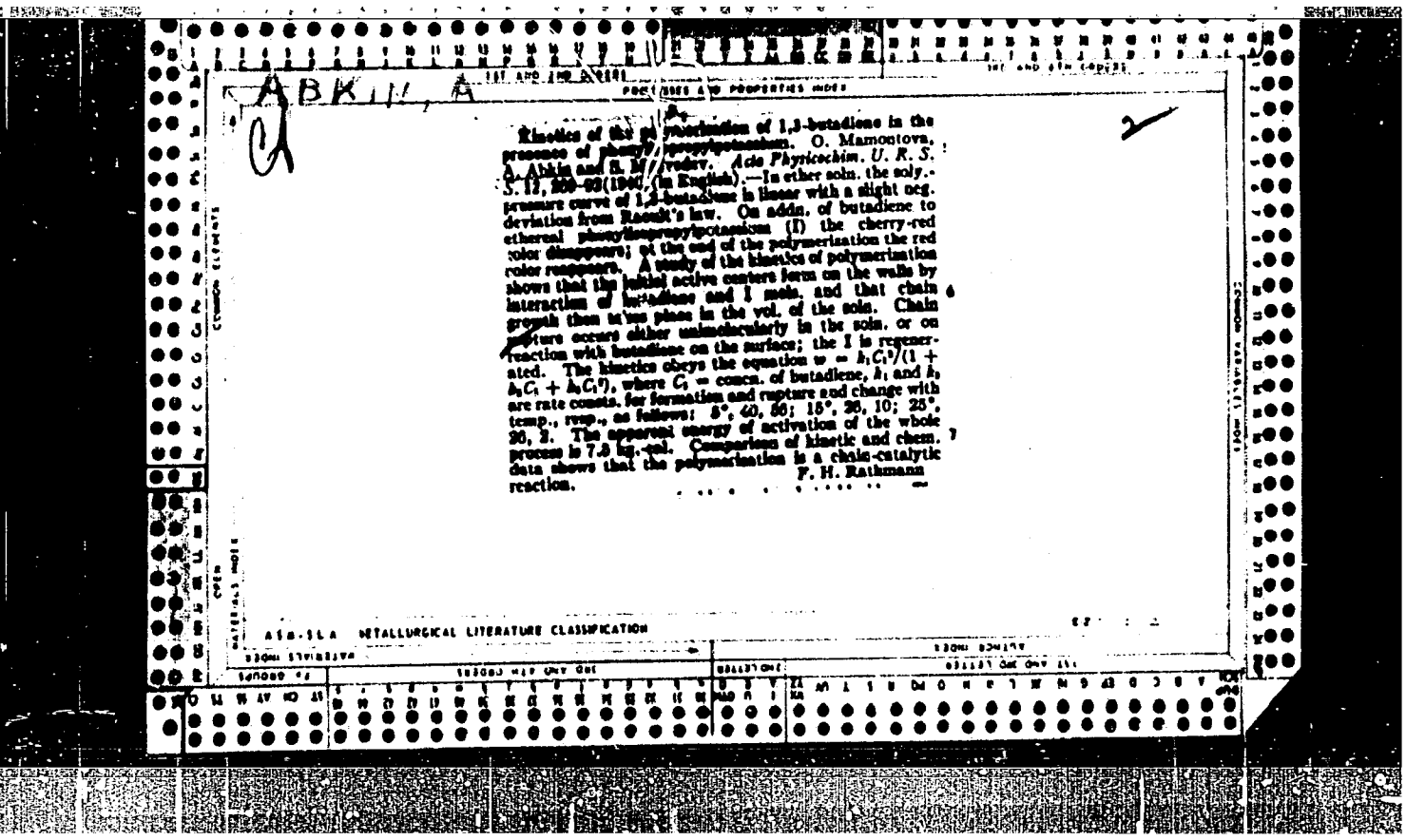

ABK II, A

Kinetics of the polymerization of 1,3-butadiene in the presence of phenyl/isopropyl/potassium. O. Mamontova, A. Abkin and S. Medvedev. *Acta Physicochim. U. R. S. S.* 12, 889-98(1940). (In English).—In ether soln. the soly.-pressure curve of 1,3-butadiene is linear with a slight neg. deviation from Raoult's law. On addn. of butadiene to ethereal phenylisopropylpotassium (I) the cherry-red color disappears; at the end of the polymerization the red color reappears. A study of the kinetics of polymerization shows that the initial active centers form on the walls by interaction of butadiene and I mols. and that chain growth then takes place in the vol. of the soln. Chain rupture occurs either unimolecularly in the soln. or on reaction with butadiene on the surface; the I is regenerated. The kinetics obeys the equation $w = k_1C_1^2/(1 + k_2C_1 + k_3C_1^2)$, where C_1 = concn. of butadiene, k_1 and k_2 are rate consts. for formation and rupture and change with temp., resp., as follows: 5°, 40, 86; 15°, 26, 10; 25°, 20, 2. The apparent energy of activation of the whole process is 7.8 kg.-cal. Comparison of kinetic and chem. data shows that the polymerization is a chain-catalytic reaction.

F. H. Rathmann

A58-51A METALLURGICAL LITERATURE CLASSIFICATION

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ARKIN, A.

RC

A-1

Kinetics of the polymerization of $\Delta^{2,3}$-butadiene in presence of potassium phenylisopropyl. O. Mamontova, A. Abkin, and S. Medvedev (*J. Phys. Chem. Russ.*, 1940, 14, 35—48).—The rate of polymerization was determined from the reduction of vol. of gaseous $(CH_2CH)_2$ (I) over a solution of $K\cdot C_6H_4Pr^{\beta}$ (II) in Et_2O, the pressure p of (I) being kept const. When p increased (between 540 and 620 mm. Hg), the rate increased at first slowly, then rapidly, and then again slowly; the highest rate at 25° was about 6 c.c. of gas per min. and per c.c. of solution. The effect of the concn. of (II) (between 10^{-3} and 6×10^{-3} N.) was indefinite. An increase of the surface area of glass in contact with solution raised the rate but < proportionately to the area. From measurements at 5°, 15°, and 25° the activation energy was calc. to be 7600 g. cal. The reaction chains probably started at the surface, grew in the bulk of solution, and broke down both at the surface and in the bulk. Saturated solutions of (I) in Et_2O are 0·3N. and 0·73N. at p_{25} = 572 and 637 mm. Hg respectively.

I. J. B.

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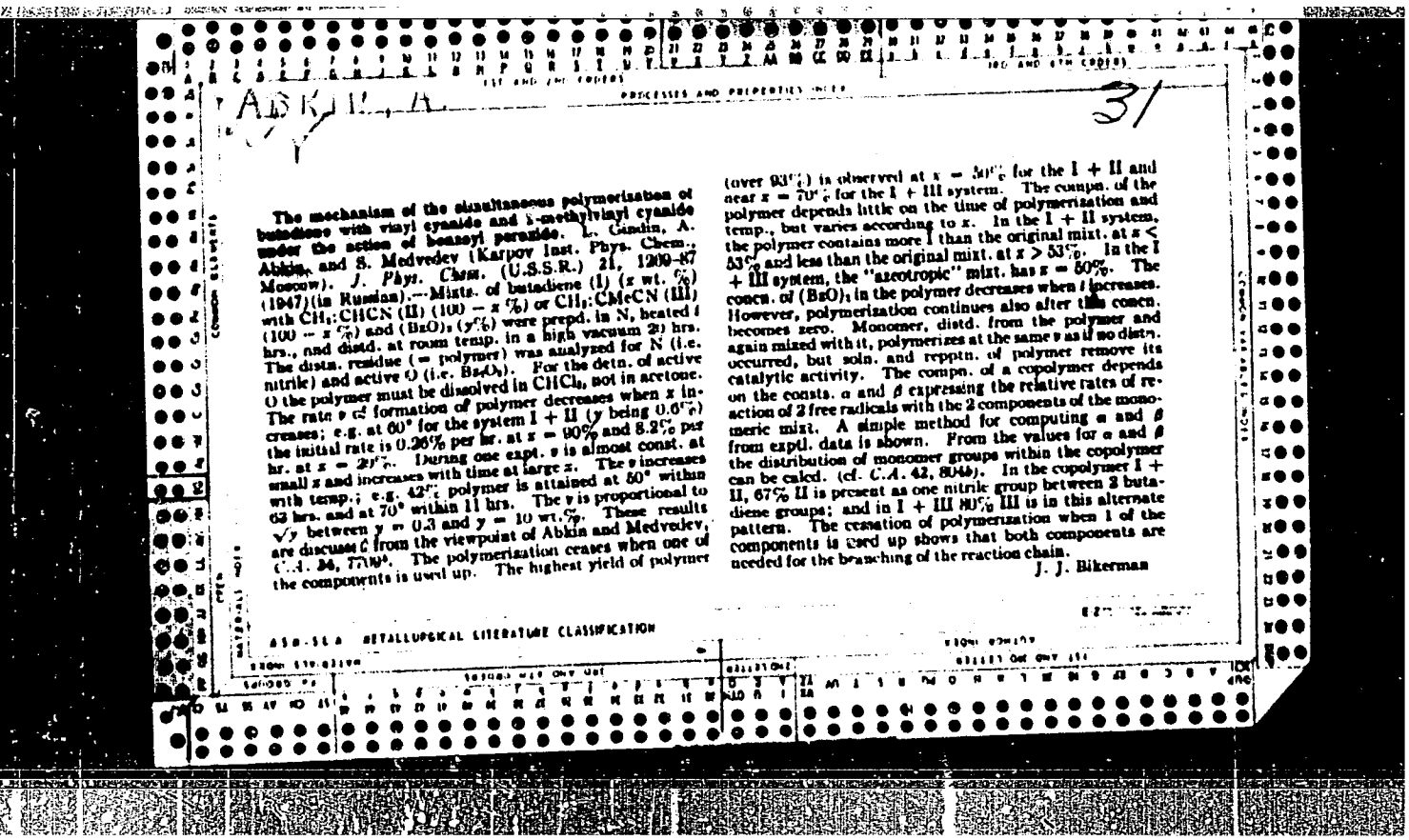

The mechanism of the simultaneous polymerization of butadiene with vinyl cyanide and α-methylvinyl cyanide under the action of benzoyl peroxide. L. Gindin, A. Abkin, and S. Medvedev (Karpov Inst. Phys. Chem., Moscow). *J. Phys. Chem.* (U.S.S.R.) 21, 1209–87 (1947)(in Russian).—Mixts. of butadiene (I) (*x* wt. %) with CH_2:CHCN (II) (100 − *x* %) or CH_2:CMeCN (III) (100 − *x* %) and $(BzO)_2$ (*y*%) were prepd. in N, heated 4 hrs., and distd. at room temp. in a high vacuum 2½ hrs. The distn. residue (= polymer) was analyzed for N (i.e. nitrile) and active O (i.e. Bz_2O_2). For the detn. of active O the polymer must be dissolved in $CHCl_3$, not in acetone. The rate *v* of formation of polymer decreases when *x* increases; e.g. at 60° for the system I + II (*y* being 0.6%) the initial rate is 0.26% per hr. at *x* = 90% and 8.2% per hr. at *x* = 20%. During one expt. *v* is almost const. at small *x* and increases with time at large *x*. The *v* increases with temp.; e.g. 42% polymer is attained at 60° within 63 hrs. and at 70° within 11 hrs. The *v* is proportional to $\sqrt{y}$ between *y* = 0.3 and *y* = 10 wt.%. These results are discussed from the viewpoint of Abkin and Medvedev, *C.A.* 34, 7709⁹. The polymerization ceases when one of the components is used up. The highest yield of polymer (over 93%) is observed at *x* = 50% for the I + II and near *x* = 70% for the I + III system. The compn. of the polymer depends little on the time of polymerization and temp., but varies according to *x*. In the I + II system, the polymer contains more I than the original mixt. at *x* < 53% and less than the original mixt. at *x* > 53%. In the I + III system, the "azeotropic" mixt. has *x* = 80%. The concn. of $(BzO)_2$ in the polymer decreases when *t* increases. However, polymerization continues also after this concn. becomes zero. Monomer, distd. from the polymer and again mixed with it, polymerizes at the same *v* as if no distn. occurred, but soln. and repptn. of polymer remove its catalytic activity. The compn. of a copolymer depends on the consts. α and β expressing the relative rates of reaction of 2 free radicals with the 2 components of the monomeric mixt. A simple method for computing α and β from exptl. data is shown. From the values for α and β the distribution of monomer groups within the copolymer can be calcd. (cf. *C.A.* 42, 8046*b*). In the copolymer I + II, 67% II is present as one nitrile group between 2 butadiene groups; and in I + III 80% III is in this alternate pattern. The cessation of polymerization when 1 of the components is used up shows that both components are needed for the branching of the reaction chain.

J. J. Bikerman

A50-51A METALLURGICAL LITERATURE CLASSIFICATION

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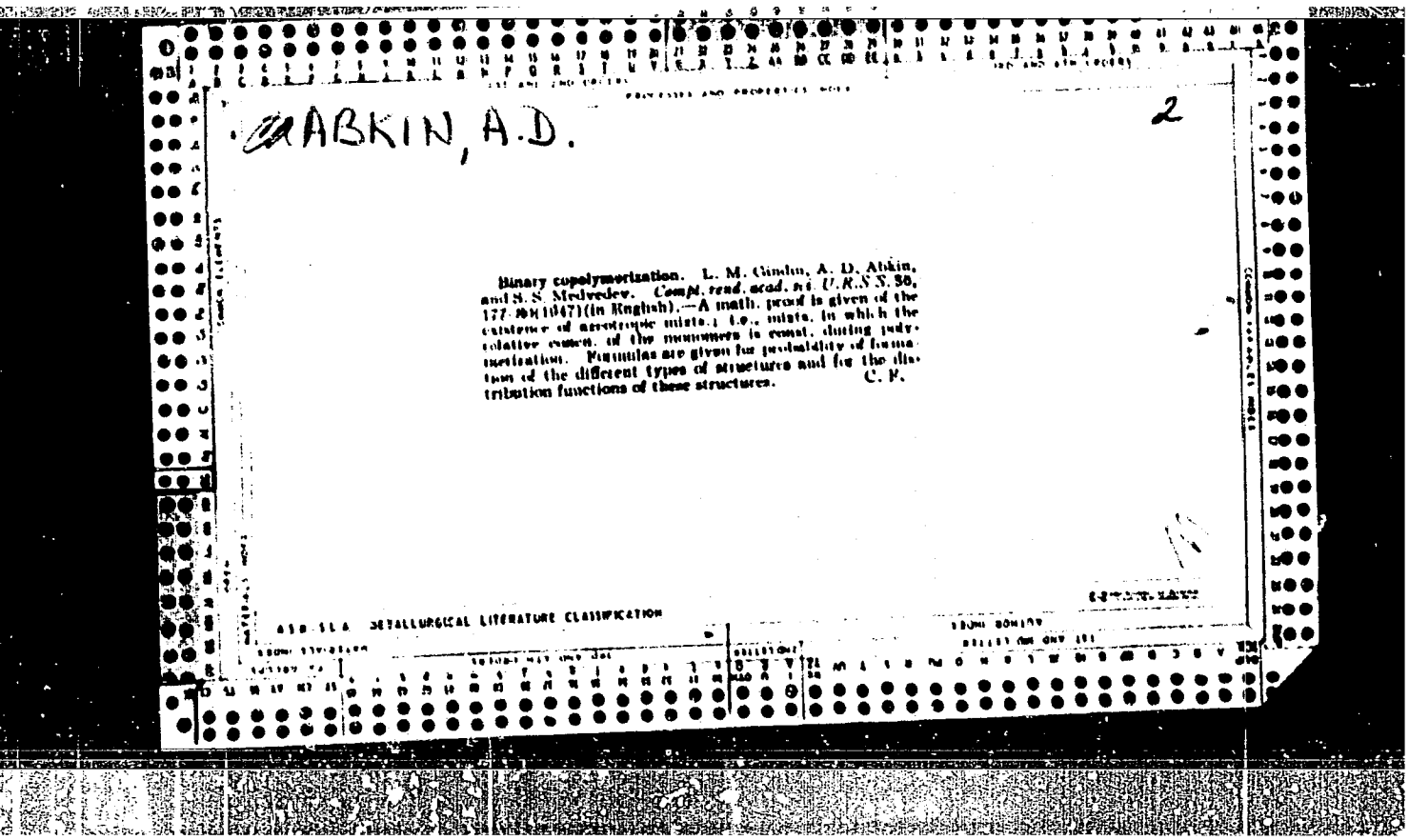

ABKIN, A.D.

2

Binary copolymerization. L. M. Gindin, A. D. Abkin, and S. S. Medvedev. *Compt. rend. acad. sci. U.R.S.S.* 56, 177-80(1947)(in English).—A math. proof is given of the existence of azeotropic mixts., i.e., mixts. in which the relative concns. of the monomers is const. during polymerization. Formulas are given for predictability of formation of the different types of structures and for the distribution functions of these structures. C. F.

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CA ABKIN, A. D.

Kinetics and mechanism of copolymerization. A. D. Abkin (L. Ya. Karpov Phys.-Chem. Inst., Moscow). *Doklady Akad. Nauk S.S.S.R.* 73, 493–6(1950).—The rate w of consumption of the sum of 2 monomers A and B can be expressed by $w = k_{AA}A \cdot A + k_{AB}A \cdot B + k_{BA}B \cdot A + k_{BB}B \cdot B$, where the symbols denote the concns., and the dots designate the corresponding polymer radicals. With $R = A \cdot + B \cdot$, and the conditions of stationariness (rate of initiation = rate of termination), this becomes $w = k_{AA}k_{BB}(r_A + r_B)^{1/2}/k_t^{1/2}(a/b)$, where r_A and r_B = rates of initiation in sep. polymerization, k_t = rate const. of termination, and $a = \alpha A^2 + 2AB + \beta B^2$, and $b = k_{AA}\beta B + k_{BB}\alpha A$, with $\alpha = k_{AA}/k_{AB}$ and $\beta = k_{BB}/k_{BA}$. In polymerization initiated by Bz_2O_2, the factor multiplying (a/b) in the above equation becomes $1.42\,(k_o'/k_t)^{1/2}\lambda(A + B)^{1/2}P^{1/2}k_{AA}k_{BB}$, where P = concn. of the peroxide, and $\lambda = k_o/k_o'$ = ratio of the rate consts. of initiation for the monomers A and B, resp. With λ known, this permits calcn. of $\delta = k_{AA}/k_{BB}$, and hence of the rates for any binary system in relative units. If, in addn. to it, the abs. value of one of the individual propagation consts., and k_t, are known, the remaining 3 propagation consts. can be calcd. from kinetic data. Such calcns. were carried out and found in agreement with literature data. At const. sum $A_0 + B_0 = C_0$, the rates of sep. polymerizations of A and of B, become, resp., $w_A = 1.42(k_o'/k_t)^{1/2}k_{AA}P^{1/2}C_0^{1/2}$ and $w_B = 1.42\,(k_o'/k_t)^{1/2}k_{BB}P^{1/2}C_0^{1/2}$, and the rate of copolymerization becomes $w = \lambda(A + B)^{1/2}(w_Aw_B/C_0^{1/2})(a/b')$, where $b' = w_A\beta B + \lambda^{1/2}w_B\alpha A$; if the rate of initiation is a quadratic function of the concns. of the monomers, the factor multiplying (a/b') is $\lambda(A^2 + B^2)(w_Aw_B/C_0^2)$. This equation permits calcn. of binary systems from the rates of sep. polymerizations; plots of w as a function of the proportions of A and of B, for different values of λ (from 0.1 to 100), constructed with the aid of this equation, were tested with satisfactory results against exptl. data for different monomer pairs. The consts. λ and δ are related by $w_A/w_B = \lambda^{1/2}\delta$. With δ and β known, the relative reactivities of different radicals can be calcd., and are found to increase in the order styrene, butadiene, methyl methacrylate, vinyl cyanide, methyl acrylate, vinyl acetate. These results lead to the following conclusions: (1) The rate of the interaction between B and A· is greater the more highly the monomer B is activated through bond delocalization, and the less stabilized the radical A·; addn. of small amts. of B reduces the total rate of polymerization sharply, and gives rise to a min. However, the rate of copolymerization can be increased through predominant initiation by one of the monomers, i.e. when $\alpha \ll 1$, $\beta \gg 1$. (2) Presence of a polar effect may create conditions favorable to an interaction between a moderately reactive A and a stabilized radical B·, depending on δ and the polar effect, addn. of B can increase the rate of copolymerization and give rise to a max. of w.

N. Thon

1951

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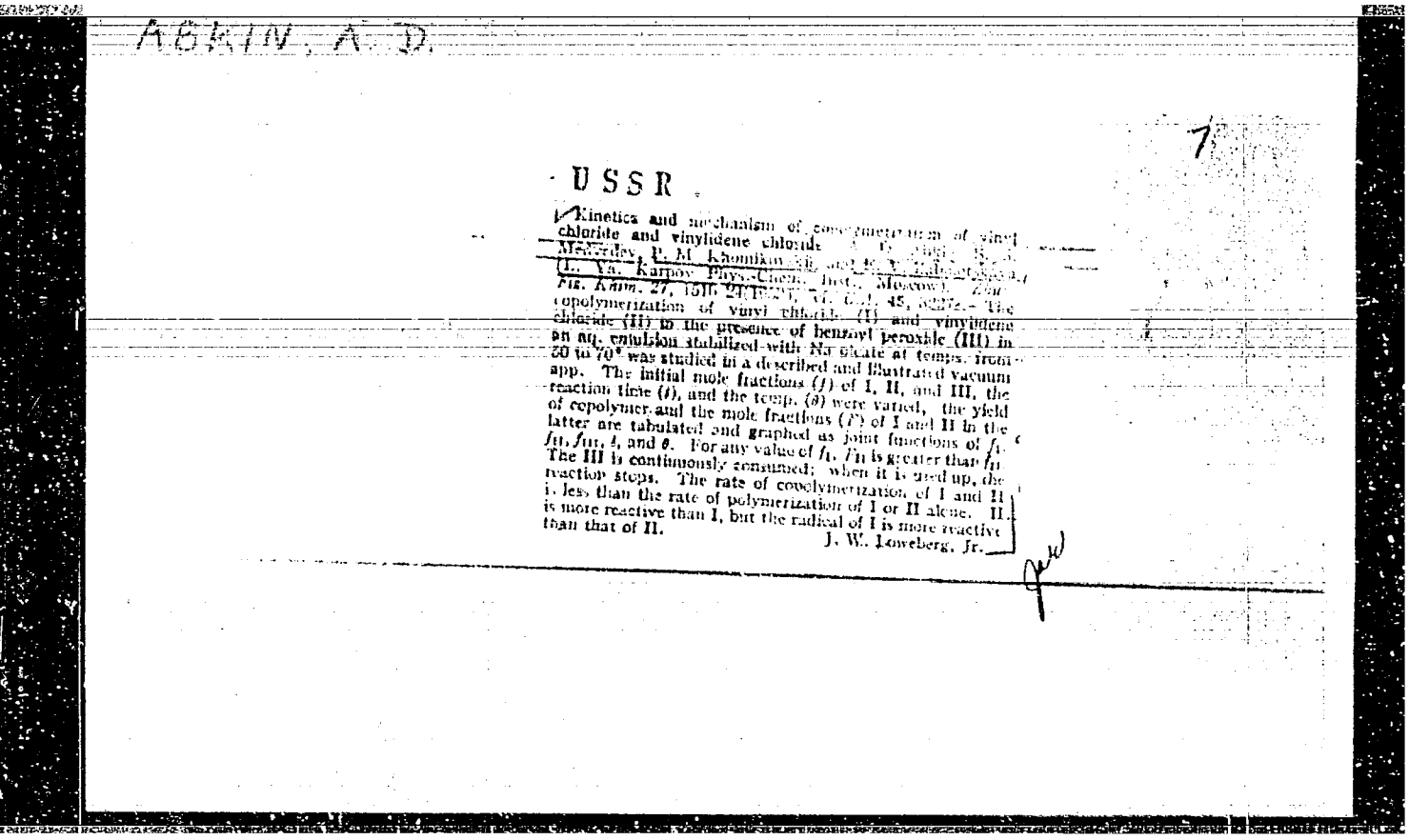

ABKIN, A. D.

7

USSR

Kinetics and mechanism of copolymerization of vinyl chloride and vinylidene chloride. [illegible] Medvedev, P. M. Khomikovskii, and [illegible] (L. Ya. Karpov Phys.-Chem. Inst., Moscow). Zhur. Fiz. Khim. 27, 1516-24(1953), [illegible] 45, [illegible].—The copolymerization of vinyl chloride (I) and vinylidene chloride (II) in the presence of benzoyl peroxide (III) in an aq. emulsion stabilized with Na oleate at temps. from 50 to 70° was studied in a described and illustrated vacuum app. The initial mole fractions (f) of I, II, and III, the reaction time (t), and the temp. (θ) were varied, the yield of copolymer and the mole fractions (F) of I and II in the latter are tabulated and graphed as joint functions of f_I, f_{II}, f_{III}, t, and θ. For any value of f_I, F_{II} is greater than f_{II}. The III is continuously consumed; when it is used up, the reaction stops. The rate of copolymerization of I and II is less than the rate of polymerization of I or II alone. II is more reactive than I, but the radical of I is more reactive than that of II.

J. W. Loweberg, Jr.

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ABKIN, A. D.

USSR/Chemistry - Polymerization Nov 53

"The Nature of the Reactions of Branching in Diene Polymerization of the Radical Type," A. D. Abkin, S. N. Kamenskaya, S. S. Medvedev, Phys-Chem Inst im L. Ya. Karpov

Zhur Fiz Khim, Vol 27, No 11, pp 1604-1609

Detd the initial velocities of polymerization of vinyl acetate (I), pentene-1 (II), and pentene-2 (III) separately as well as in copolymerization of I with II and III. On the basis of the initial velocities, detd the consts of copolymerization. Found that pentenes inhibit polymerization of I. Estimated the relative velocities of interaction of pentenes with radicals of I, styrene, and butadiene. Found that branching in the polymerization of butadiene-1,3 is caused by chain transfer.

274T15

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ABKIN, A. D.

The Nature of the Branching Reaction During Radical Polymerization of Dienes. A. D. Abkin, S.N. Kamenskaya, S.S.Medvedev, Cor. Mbr.,Acad. Sci.USSR; Sci. Res. Physicochem. Inst. im. L. Ya. Karpov - DAN SSSR, vol.86,no.2, Jan 53, pp 269-271

A Quant appraisal is made of the specific rates of the reaction between the polybutadiene radical and polybutadiene particles at the mono- and di-substituted double bond.

255T15

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Abkin, AD

The kinetics of copolymerization. A. D. Abkin. *Vop. rezy Khim. Kinetiki, Katalizu i Reaktsionnoi Sposobnosti, Akad. Nauk S.S.S.R.* 1955, 338–52.—Copolymerization problems can be studied much more fully on the basis of kinetic data on copolymerization reactions (Abkin, *et al.*, *C.A.* 49, 4525b, 5058e) than merely from the quant. relations of the various polymer formations and the distribution of the monomer units in the mol. The method and results of kinetic investigation are discussed. An equation derived for the velocity of polymerization reaction gives sufficiently accurate information on the shape of the velocity-compn. curve for any real binary system and gives the value of a const. that characterizes the effectiveness of a "crisscross" chain rupture. Monomers with conjugated double bonds were found to be most reactive towards radicals of any type, whereas monomers with isolated double bonds are least reactive toward radicals. This is illustrated on the vinyl chloride + butadiene, vinyl chloride + vinylidene chloride, vinyl acetate + styrene, etc., polymerizations. A table was constructed of the relative reactivities of monomers and radicals, and the reasons for the reactivity differences are discussed on the basis of their chem. structures.

W. M. Sternberg

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M. A. YOUTZ
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ABKIN, A. D., and SOKOLOV, L. B.

"General theory of addition polymerization," a paper presented at the 9th Congress on the Chemistry and Physics of High Polymers, 28 Jan-2 Feb 57, Moscow, Karpov Inst.

B-3,084,395

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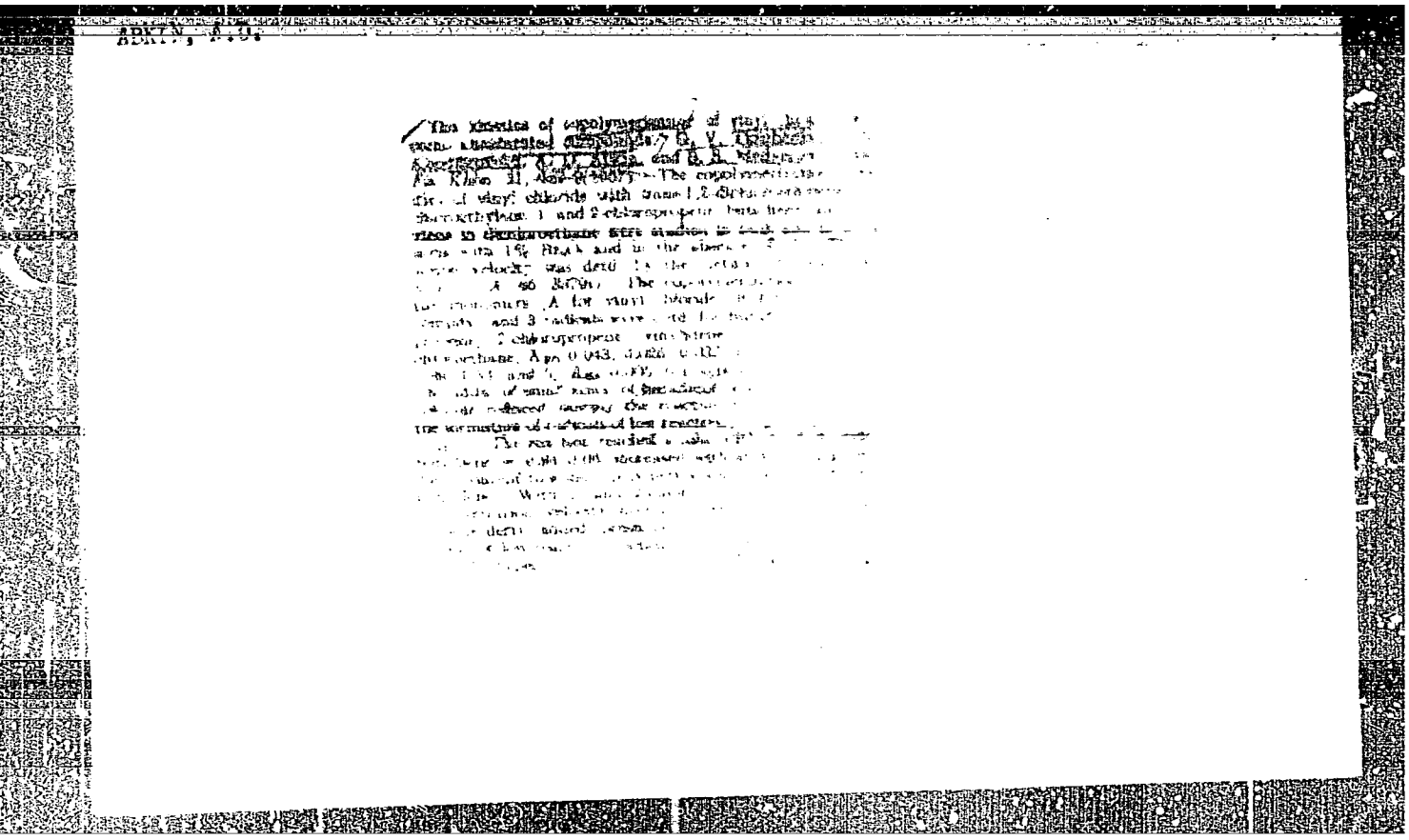

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SOKOLOV, L.B.; ARKIN, A.D.

Additivity of contraction in copolymerization. Vysokom. soed. 1 no.6: 863-864 Je '59. (MIRA 12:10)

1.Fiziko-khimicheskiy institut im. L. Ya. Karpova.
(Polymerization)

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SOKOLOV, L.B.; ABKIN, A.D.

Copolymerization with the participation of bifunctional manomers.
Vysokom.soed. 1 no.7:1024-1026 Jl '59. (MIRA 12:11)

1. Fiziko-khimicheskiy institut im L.Ya. Karpova.
(Polymerization)

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DYURNBAUM, V.S.; ABKIN, A.D.; KLIMENKOV, V.S.

Production of copolymers of acrylonitrile with methacrylamide and of fibers derived from them. Khim. volok. no.2:24-28 '59.
(MIRA 12:9)

1.Vsesoyuznyy nauchno-issledovatel'skiy institut iskusstvennogo volokna.
(Acrylonitrile) (Methacrylamide) (Rayon)

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5(4) SOV/76-33-6-34/44

AUTHORS: Sokolov, L. B., Abkin, A. D.

TITLE: On the Mechanism of Copolymerization With Participation of Bifunctional Monomers (O mekhanizme sovmestnoy polimerizatsii s uchastiyem bifunktsional'nykh monomerov). I. Copolymerization of α-Chloracrylate of 2-Ethoxyethanol With Styrene, Methylmethacrylate and Methylacrylate (I. Sovmestnaya polimerizatsiya α-khlorakrilovogo efira 2-etoksietanola so stirolom, metilmetakrilatom i metilakrilatom)

PERIODICAL: Zhurnal fizicheskoy khimii, 1959, Vol 33, Nr 6, pp 1387-1392 (USSR)

ABSTRACT: In connection with the problems of synthesis of branched and reticular polymers (P), investigations of the polymerization mechanism of systems with binfunctional monomers are particularly important. The copolymerization (CP) of the monomers styrene (I), methylmethacrylate (II) and methylacrylate (III) with ethylene-glycol-di-α-chloracrylate (IV) and 2-ethoxyethanol-α-chloracrylate (V) was investigated. The present paper presents the experimental results obtained with (V). The (CP) took place in methylethylketone solutions at 50°C. Benzoylperoxide was used as initiator, and the re-

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On the Mechanism of Copolymerization With Participation of Bifunctional Monomers. I. Copolymerization of α-Chloracrylate of 2-Ethoxyethanol With Styrene, Methylmethacrylate and Methylacrylate

action kinetics was determined by the dilatometric method. On the system (III) - (V) it was observed that (V) is a more active monomer than (III) but much less active than the radical. The (CP)-constants computed for this system are $\alpha = 0.1$ and $\beta = 3.8$. A closer consideration of the reaction mechanism is put forward. In the (CP) of (II) with (V) there was computed $\alpha = 0.4$ and $\beta = 1.2$, and in contrast to the system (III) - (V), a weak maximum was observed in the diagram polymerization rate (PR) - composition (Fig 2). The latter is due to polar factors. For the system (I) - (V), the values $\alpha = 0.12$ and $\beta = 0.26$ were obtained which point to the fact that (I) is more active than (V) in the reaction with the monoester radical. In the diagram (PR) - composition (Fig 3), a distinctly marked maximum can be observed which is also produced by a polar effect. A comparison of the (CP)-constants obtained with those of the system with methyl-α-chloracrylate (Refs 8-10) (Table) shows good agreement. It is ascertained that the polymerization kinetics of the systems investigated can be well represented by the simplified equation of the

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SOV/76-33-6-34/44

On the Mechanism of Copolymerization With Participation of Bifunctional Monomers. I. Copolymerization of α-Chloracrylate of 2-Ethoxyethanol With Styrene, Methylmethacrylate and Methylacrylate

copolymerization kinetics, under the assumption of equal initiation rates of the process on both monomers. Finally, the authors express their thanks to Academician S. S. Medvedev. There are 3 figures, 1 table, and 17 references, 8 of which are Soviet.

ASSOCIATION: Fiziko-khimicheskiy institut im. L. Ya. Karpova, Moskva (Physico-chemical Institute imeni L. Ya. Karpov, Moscow)

SUBMITTED: December 13, 1957

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5 (4), 15 (8)

AUTHORS: Sokolov, L. B., Abkin, A. D. SOV/76-33-7-9/40

TITLE: On the Mechanism of Copolymerization With Participation of Bifunctional Monomers. II. Particularities of the Polymerization of Binary Systems With the Participation of the Ethylene Glycol Di-α-chloroacryl Ester

PERIODICAL: Zhurnal fizicheskoy khimii, 1959, Vol 33, Nr 7, pp 1495 - 1503 (USSR)

ABSTRACT: The authors investigated the copolymerization (CP) of the ethylene glycol di-α-chloroacryl ester (I) (diester) with styrene (II), methyl methacrylate (III), and methyl acrylate (IV). (I) was obtained from α-chloro acrylic acid and ethylene glycol by a method described already earlier (Ref 1). The authors checked the polymerization (P) at 50 ± 0.05°C in methyl-ethyl ketone at a monomer concentration of 1 mol/l. During the (P) of (I) it was found that the polymer is precipitated by (P) of 3 or 4%. For the (CP) of (IV) with (I) the (CP)-constants $\alpha = 0.1$ and $\beta = 3.6$ were obtained; for the (CP) of (III) with (I), $\alpha = 0.35$ and $\beta = 1.4$, and for the (CP) of (II) with (I), $\alpha = 0.01$ and $\beta = 0.2$. Accordingly, the authors found the following: The (P)-rate of (I) is twice as great as that of the

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On the Mechanism of Copolymerization With Participation of Bifunctional Monomers. II. Particularities of the Polymerization of Binary Systems With the Participation of the Ethylene Glycol Di-α-chloroacryl Ester SOV/76-33-7-9/40

monoester. By the method of light dispersion it was found (Table) that ramified and reticular copolymers are formed during the (CP) of (I). In the initial stage of (CP), the reactivity of the vinyl groups of (I) is equal to the reactivity of the vinyl groups of the monoester. A characteristic feature of the (CP) of the systems (IV) + (I) and (III) + (I), i.e. with bifunctional monomers like (I), is its low separation rate, which is ascribed to the reticular structure of the resultant copolymer and regarded as a specific phenomenon of the reaction kinetics of systems with bifunctional monomers. For investigations of the particularities of the system it is assumed that the reaction acceleration with time is to be explained by an accumulation of radicals within the system, which is caused by chain transfer on the part of the polymer, or by an initiation reaction of the added vinyl groups. In conclusion, the authors thank Academician S. S. Medvedev for his assistance.

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On the Mechanism of Copolymerization With Participation of Bifunctional Monomers. II. Particularities of the Polymerization of Binary Systems With the Participation of the Ethylene Glycol Di-α-chloroacryl Ester

SOV/76-33-7-9/40

There are 5 figures, 1 table, and 12 references, 4 of which are Soviet.

ASSOCIATION: Fizikokhimicheskiy institut im. L. Ya. Karpova (Physico-chemical Institute imeni L. Ya. Karpov)

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APPROVED FOR RELEASE: 04/03/2001 CIA-RDP86-00513R000100130002-4"

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5.3831

66876

~~5(4)~~ SOV/76-33-11-47/47

AUTHORS: Abkin, A. D., Sheynker, A. P., Mezhirova, L. P.

TITLE: On the "Carbanion" Mechanism of Polymerization Under the Effect of Gamma Rays

PERIODICAL: Zhurnal fizicheskoy khimii, 1959, Vol 33, Nr 11, p 2636 (USSR)

ABSTRACT: Data from publications (Ref 1) on the polymerization of isobutylene, and data of the joint polymerization of isobutylene with vinylidene chloride and of the styrene with methyl methacrylate, obtained by the authors (Ref 2) show that at low temperatures and influenced by nuclear radiation, the polymerization occurs according to the carbonium mechanism. Up to present there is no information in publications on the course of a "carbanion" mechanism at the polymerization under the influence of nuclear radiation. It has been established that the polymerization may proceed according to both mechanisms (carbonium or "carbanion" mechanism) and that this is not determined by the chemical structure of the monomers, but by the nature of the medium. Data on the polymerization of acrylic acid nitrile and styrene at -78°C (Table) under the influence

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On the "Carbanion" Mechanism of the Polymerization Under the Effect of Gamma Rays

of gamma rays, show that the polymerization of the acrylic acid nitrile in solving agents with electron donor substituents (triethyl amine, dimethyl formamide) occurs and that none occurs in ethyl chloride (which is usually used for carbonium polymerization) containing electrophilic groups. Contrary, styrene polymerizes only in ethyl chloride. These data show that acrylic acid nitrile, which has molecules containing electronegative groups, polymerizes, under the given conditions, not according to the radical mechanism, but according to the "carbanion" mechanism. It is mentioned that more detailed results of the investigations carried out will be published later and that the authors thank Academician S. S. Medvedev. There are 1 table and 3 references, 2 of which are Soviet.

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"APPROVED FOR RELEASE: 04/03/2001 CIA-RDP86-00513R000100130002-4

5(4)

AUTHORS: Sheynker, A. P., Yakovleva, M. K., Kristal'nyy, E. V., Abkin, A. D.

SOV/20-124-3-39/67

TITLE: On the Mechanism of the Low-temperature Polymerization of Monomers Under the Action of a Gamma-radiation (O mekhanizme nizkotemperaturnoy polimerizatsii monomerov pod deystviyem gamma-izlucheniya)

PERIODICAL: Doklady Akademii nauk SSSR, 1959, Vol 124, Nr 3, pp 632-634 (USSR)

ABSTRACT: The present paper deals with the results obtained by investigating the mechanism of the low-temperature polymerization of various vinyl compounds under the action of a γ-radiation. The authors investigated this mechanism by employing the method of joint polymerization, according to which it is possible to obtain the necessary information concerning the nature of active particles (radicals, ions) participating in the active process from the composition of the Ko-polymer and from the kinetic data. The authors investigated the common polymerization of isobutyls with vinylidene chloride (in the "mass") in the temperature interval of -78 to 0°,

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On the Mechanism of the Low-temperature Polymerization of Monomers Under the Action of a Gamma-radiation

and of methyl-metacrylate with styrene in ethylchloride as solvent at -78 to +25°. Polymerization was carried out in ampoules on a Co^{60}-source of 20,000 g-equivalents at an intensity of 230-250 r/sec. The degree of polymerization was not more than 10%. A diagram supplies data concerning the dependence of the copolymers on the composition of the original mixture for the system isobutylene-vinylidene chloride, which were determined in the course of polymerization at different temperature conditions. From these data the constants of the common polymerization α (for isobutylene) and β (for vinylidene chloride) were then determined according to the simplified equation for the integral composition. The following holds:

Polymerization temperature in °C	α	β
-78	25	0
-40	1.27	0.21
0	0.03	1.3

Card 2/4 The composition of the common polymers formed depend to a

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On the Mechanism of the Low-temperature Polymerization of Monomers Under the Action of a Gamma-radiation

considerable extent on temperature. Details are given. The data discussed in the present paper permit the following conclusions to be drawn: The joint polymerization of isobutylene with vinylidene chloride under the influence of a γ-radiation at low temperatures occurs according to the carbonium (karboniyeviy) mechanism or a similar mechanism. The authors further investigated the polymerization of styrene in an equimolecular mixture of styrene and methyl metacrylate in ethyl chloride as solvent. With decreasing temperature, the methyl metacrylate component in the copolymer decreases, which indicates an increase of the share of ion reactions in this process. The authors thank Academician S. S. Medvedev for discussing the results obtained. There are 2 figures, 2 tables, and 8 references, 4 of which are Soviet.

ASSOCIATION: Nauchno-issledovatel'skiy fiziko-khimicheskiy institut im. L. Ya. Karpova (Physico-Chemical Scientific Research Institute imeni L. Ya. Karpov)

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SOV/20-124-3-39/67

On the Mechanism of the Low-temperature Polymerization of Monomers Under the Action of a Gamma-radiation

PRESENTED: October 30, 1958, by S. S. Medvedev, Academician

SUBMITTED: October 27, 1958

Card 4/4

APPROVED FOR RELEASE: 04/03/2001 CIA-RDP86-00513R000100130002-4"

"APPROVED FOR RELEASE: 04/03/2001 CIA-RDP86-00513R000100130002-4

ABKIN, A. D., SHEYNKER, A. P., YAKOVLEVA, M. K., MEZHIROVA, L. P.

"On the carbonium and carbonion mechanisms of gamma-ray induced polymerization." report presented at the International Polymer Symposium, (IUPAC), Moscow, USSR, 14-18 June 1960.

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"APPROVED FOR RELEASE: 04/03/2001 CIA-RDP86-00513R000100130002-4

S/081/61/000/021/085/094
B145/B144

AUTHORS: Rozovskaya, N. N., Abkin, A. D.

TITLE: Study of the copolymerization of styrene and α-eleostearic acid

PERIODICAL: Referativnyy zhurnal. Khimiya, no. 21, 1961, 456, abstract 21P115. (Lakokrasochn. materialy i ikh primeneniye, no. 1, 1961, 9 - 12)

TEXT: The copolymerization of styrene (I) and α-eleostearic acid (II) dissolved in toluene was studied in the presence of benzoyl peroxide. Methods and results are presented. The copolymerization constants were determined, the differential and integral compositions of the polymers in the course of polymerization were calculated, and the conditions under which the copolymerization limit is reached were established. Small additions of II were found to inhibit the polymerization of I considerably. As a monomer, II is more reactive than I even though the reactivity of the radical of I is much higher than that of the radical of II. This fact causes

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S/081/61/000/021/085/094
Study of the copolymerization of styrene ... B145/B144

the inhibitory action of II on the polymerization of I. [Abstracter's note: Complete translation.]

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"APPROVED FOR RELEASE: 04/03/2001 CIA-RDP86-00513R000100130002-4

33125
S/638/61/001/000/056/056
B125/B104

IS 8620

AUTHORS: Sheynker, A. P., Abkin, A. D.

TITLE: Ion mechanism of polymerization under the action of nuclear radiations

SOURCE: Tashkentskaya konferentsiya po mirnomy ispol'zovaniyu atomnoy energii. Tashkent, 1959. Trudy. v 1. Tashkent, 1961, 395-400

TEXT: The copolymerization of the following pairs of monomers was examined: isobutylene - vinylidene chloride (in the bulk) between -78 and 0°C; styrene - methyl methacrylate between -78° and 25°C; and isobutylene - styrene at -78°C (with ethyl chloride as solvent); acrylonitrile - styrene at -78°C (as solution in dimethyl formamide) Specially designed dilatometers and a Co^{60} source were used for the experiments. The copolymerization constants r_1 (for isobutylene), and r_2 (for vinylidene chloride) at -70, -40, and 0°C are 25, 1.27, 0.03, and 0, 0.21, 1.3, respectively. The compositions of the resulting copolymers are largely dependent on the polymerization temperature, and their concentration rises

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Ion mechanism of polymerization ...

significantly on cooling from -40 to -78°C. Therefore, low- and high-temperature polymerization under the action of radiation probably follow the ion and the radical mechanism, respectively. On the strength of these and other facts, gamma irradiation permits low-temperature copolymerization of isobutylene with vinylidene chloride according to the carbonium mechanism. The radiation polymerization of styrene and methyl methacrylate at 25°C follows the radical process. In the gamma polymerization of an equimolecular mixture of styrene and methyl methacrylate in ethyl chloride, the relative amount of the methyl methacrylate component in the copolymer drops rapidly with decreasing polymerization temperature. The resulting copolymers contain a component with a high concentration of styrene. Ion chains are formed in the low-temperature polymerization of styrene and methyl methacrylate according to the carbonium mechanism. The polymerization rate is reduced sharply by the addition of small amounts of isobutylene to styrene. Low-temperature radiation polymerization may also take place according to the ion mechanism. Not only the chemical structure of the monomer to be polymerized, but also the nature of the surrounding medium influences the polymerization mechanism. The mechanism of ion chain formation and the nature of the resulting ion pairs will later be studied. M. K. Yakovleva and L. P Mezhirova assisted in the investiga-

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33125
S/638/61/001/000/056/056
B125/B104

Ion mechanism of polymerization ...

tion. Academician S. S. Medvedev is thanked for interest. There are 5 figures, 2 tables, and 14 references: 7 Soviet and 7 non-Soviet. The four most recent references to English-language publications read as follows: Davison W. H. G., Pinner S. H., Worrall R., Chem. a Ind. 38, 1274, 1957; Worrall R., Charlesby A., Journ.. Appl. Rad. a Isot. 4. 84, 1958; Worrall R., Pinner S. H., J. Pol. Sci., 34 N 127, 229, 1959. Burlant W. J., Green D. H., J. Pol. Sci., 31, 122, 227, 1958.

ASSOCIATION: N.-i-fiziko-khimicheskiy institut im. L. Ya. Karpova (Scientific Physicochemical Research Institute imeni L. Ya. Karpov)

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"APPROVED FOR RELEASE: 04/03/2001 CIA-RDP86-00513R000100130002-4

DYURNBAUM, V.S.; ABKIN, A.D.; KLIMENKOV, V.S.

Kinetics of copolymerization of acrylonitrile with some vinyl monomers. Khim.volok. no.3:8-11 '61. (MIRA 14:6)

1. Vsesoyuznyy nauchno-issledovatel'skiy institut iskusstvennogo volokna.

(Acrylonitrile) (Vinyl compounds)

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88731

S/190/61/003/001/015/020
B119/B216

11.2210

AUTHORS: Mezhirova, L. P., Sheynker, A. P., Abkin, A. D.

TITLE: The carbanionic mechanism of polymerization under the action of gamma rays

PERIODICAL: Vysokomolekulyarnyye soyedineniya, v. 3, no. 1, 1961, 99-104

TEXT: The present work studies the polymerization of acrylonitrile and its copolymerization with styrene under the action of γ-radiation at low temperatures for the purpose of explaining the reaction mechanism. Co^{60} was used as radiative source. The experimental temperatures ranged from -50 to -112°C. Polymerization was performed in the solvents dimethyl formamide, triethyl amine, isopropyl amine, acetone, toluene, acetonitrile, propionitrile, ethyl chloride, heptane, ethyl acetate. The reaction rate was measured dilatometrically. (The volume change of the reaction mixture during polymerization was measured by the change of electric resistance of a platinum wire and a mercury thread inside the dilatometer capillary). The acrylonitrile polymers were separated from their solutions by means of

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The carbanionic mechanism of...

methyl alcohol and the styrene copolymers by a heptane - ether mixture. The copolymers were microanalyzed for C, H and N. In some cases the results were checked by infrared spectroscopy. At -78°C, and a dose rate of 128 rad/sec, the polymerization rate of acrylonitrile (initial concentration 3.5 mol/l) was 1.57 mol/l·sec·10^6 in isopropyl amine, 6.7 mol/l·sec.10^6 in triethyl amine, 9.7 mol/l·sec·10^6 in dimethyl formamide and 2.1 mol/l·sec·10^6 in the "bulk". The copolymerization constants were r_1 = 33 (acrylonitrile), r_2 = 0.'005 (styrene). Results: Acrylonitrile polymerization occurs only in the solvents dimethyl formamide, triethyl amine and isopropyl amine, but not in solvents with electron acceptor properties. The composition of the copolymers obtained at -78°C by the above method and that of the analogous copolymers prepared by a radical reaction exhibit significant differences. The polymerization rate of acrylonitrile increases proportionately with the dose rate. A reduction of the reaction temperature from -50 to -112°C produces a great increase of reaction rate and molecular weight. The findings indicate a carbanionic reaction mechanism. The authors thank Ya. A. Tsarfin and K. G. Nogteva, both at Vladimirskiy nauchno-

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B119/B216

The carbanionic mechanism of...

issledovatel'skiy institut sinteticheskikh smol (Vladimir Scientific Research Institute of Synthetic Resins) for carrying out the elementary analyses. There are 4 figures, 2 tables, and 8 references: 5 Soviet-bloc, and 3 non-Soviet-bloc.

ASSOCIATION: Fiziko-khimicheskiy institut im. L. Ya. Karpova (Physico-chemical Institute imeni L. Ya. Karpov)

SUBMITTED: June 9, 1960

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APPROVED FOR RELEASE: 04/03/2001 CIA-RDP86-00513R000100130002-4"

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22564

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S/190/61/003/005/007/014
B101/B218

AUTHORS: Sheynker, A. P., Abkin, A. D.

TITLE: Study of the mechanism of polymerization by radiation. I. Mechanism of carbonium polymerization of isobutylene and styrene under the influence of gamma radiation

PERIODICAL: Vysokomolekulyarnyye soyedineniya, v. 3, no. 5, 1961, 716-722

TEXT: The authors studied the kinetics and mechanism of separate and joint polymerization of styrene and isobutylene under the action of gamma radiation. According to published data, these monomers polymerize at low temperature following the carbonium mechanism. The kinetics of the process was studied dilatometrically. Isobutylene and styrene (2.5 moles/l) dissolved in ethylchloride were filled into reaction ampoule 1 (equipped with spiral capillary 2; Fig. 1) until the level A was reached. This process was carried out in vacuo and at the same temperature at which polymerization was performed. Capillary 3 was filled with Hg. In order to prevent boiling of the reaction mixture, sphere 5 was filled with the same mixture so that a counterpressure existed. The platinum wire 4 with the contacts 7 was con-

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Study of ...

nected to a measuring bridge and, thus, the resistance was measured, which increased due to a decrease in volume during polymerization and simultaneous lowering to the Hg level in capillary 3. The mercury was collected in 6. Irradiation was carried out with Co^{60} at -78°C and a dosage of 106 rad/sec. Volume changes not caused by polymerization (i.e., due to heating during radiation adsorption) were corrected by a control dilatometer filled with ethylchloride, isopentene, and ethylbenzene. The composition of the copolymers was determined by Ya. A. Tsarfin and K. G. Nogteva (analiticheskaya laboratoriya Vladimirskogo NIISa; Analytical Laboratory of Vladimir NIIS) by elementary analysis. Fig. 5 shows the composition of copolymers consisting of isobutylene and styrene. During the initial stage of copolymerization, the yield of copolymer is a linear function of time. The same holds for separate polymerization of monomers: styrene $20.1 \cdot 10^{-6}$ mole/l·sec; isobutylene $14.1 \cdot 10^{-6}$ mole/l·sec. Fig. 7 shows the copolymerization rate ω for different molar fractions of isobutylene. Fig. 9 presents $\log \omega$ as a function of the logarithm of the radiation dose I (14-110 rad/sec). Also $\log \omega = f(\log c)$ (c = concentration is a linear function for both monomers. The authors calculated the reaction constants from the data on the composition of the copolymers: r_1 (isobutylene) = 3.5; r_2 (styrene) = 0.33. In radiation polymerization and at low temperature,

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isobutylene is more active than styrene. Polymerization proceeds according to the carbonium mechanism, similar to that in the presence of $SnCl_4$. The molecular weights of the copolymers were determined by N. V. Nikletsova and found to be: ratio isobutylene : styrene in initial mixture: 1.0 : 0.0 0.9 : 0.1 0.5 : 0.5 0.1 : 0.9 0.0 : 1.0; molecular weight: 80,000 55,000 27,000 35,000 70,000.
As is shown in Fig. 10, copolymerization at 0°C takes an entirely different course. In this case, the radical mechanism comes in play, but this does not lead to polymerization of isobutylene. The polymers obtained at 0°C contained chlorine. There are 10 figures and 25 references: 8 Soviet-bloc and 17 non-Soviet-bloc. The 4 most important references to English-language publications read as follows: R. Worrell, S. H. Pinner, J. Polymer. Sci., 34, 229, 1959; W. H. J. Davison, S. H. Pinner, R. Worrell, Proc. Roy. Soc., A 252, 187, 1959; A. S. Hoffmann, J. Polymer Sci., 34, 241, 1959; F. S. Dainton, J. Polymer. Sci., 34, 241, 1959.

ASSOCIATION: Fiziko-khimicheskiy institut im. L. Ya. Karpova (Physico-chemical Institute imeni L. Ya. Karpov)

SUBMITTED: July 21, 1960

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S/190/61/003/006/005/019
B110/B216

11.2210 also 2209

AUTHORS: Yakovleva, M. K., Sheynker, A. P., Abkin, A. D.

TITLE: Studies of the mechanism of radiation polymerization. II. Mechanism of carbonium polymerization of styrene and methyl methacrylate under the action of γ rays

PERIODICAL: Vysokomolekulyarnyye soyedineniya, v. 3, no. 6, 1961, 828-832

TEXT: Previous studies of the authors (Ref. 1: Dokl. AN.SSSR, 124, 632, 1959) lead to the assumption that chains with ionic character form during copolymerization of an equimolar mixture of styrene and methyl methacrylate in ethyl chloride under the action of γ rays. The present work studies this influence in greater detail. Methyl methacrylate, treated with 3 % soda solution, was washed with water, dried over Na_2SO_4, distilled at 42.5°C and 101 mm Hg and stored in sealed evacuated ampules over dry ice. The kinetics of the process were determined dilatometrically, the polymerization at 25, 0, 40°, and -78°C. The polymer was separated a) by removing the solvent and unreacted monomer in vacuo in the presence

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B110/B216

Studies of the mechanism of radiation. .

of $CuSO_4$, and b) by precipitating the polymer by means of methyl alcohol in the presence of hydroquinone. The composition of the copolymer was determined by ultimate analysis for carbon and hydrogen carried out in the Vladimirskiy NIIS by Ya. A. Tsarfin and K. G. [illegible]. The infrared spectrum was taken in a solution containing 10 g of polymer to 1 l of CCl_4 at a thickness of [illegible] mm, with bands at 1725 cm^{-1} (CO group) and 700 cm^{-1} (benzene rings of polystyrene). Table 1 gives the copolymers obtained in 4.03 mole/l of ethyl chloride (isolated by methods). The copolymers prepared in this way could contain radiolytic by-products of the reaction mixtures. The copolymers prepared by b) (Fig. 2) contain more of the styrene component than those prepared by a). This is due to the formation of a low-molecular, non-volatile, CH_3OH soluble product containing more of the methyl methacrylate component than the copolymer prepared by b). It contained chlorine, had a molecular weight of 361 and showed strong absorption at 17[illegible] cm^{-1} (CO group) and 700 cm^{-1} (benzene ring). The initial polymerization rate was determined from the curve sections in Fig. 4. Fig. 5 shows the dependence of styrene and methyl methacrylate polymerization on the composition of the initial monomer mixture. The

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styrene concentration is a linear function of the monomer concentration. Table 2 illustrates the dependence of the styrene polymerization rate on the surface of the reaction vessel. At -78°C, the use of ampoules made of stainless steel reduced the rate of styrene polymerization. The polymer molecular weights at an initial molar ratio styrene : methyl methacrylate of 0.9:0.1 were determined by N. V. Makletsova by the light scattering method at 70,000 for polystyrene and 30,000 for the copolymer. In copolymerization under the action of γ-radiation, lowering of the reaction temperature from 25°C to -78°C increases the relative content of styrene component (r_1(styrene) = 20; r_2 = 0.005). On polymerization of these monomers under the action of γ-radiation at 25°C, r_1 = 0.63; r_2 = 0.50. In the case of a peroxide-initiated polymerization at 60°C, r_1 = 0.52; r_2 = 0.46. With cation catalysts, r_1 = 10.5; r_2 = 0.1 and with anion catalysts r_1 = 0.1; r_2 = 6.0. The copolymer composition and the dependence of the copolymerization rate on the composition of the monomer mixture (Fig. 5) indicate a carbonium mechanism of polymerization of styrene with methyl methacrylate at low temperatures under the action of γ rays. Fig. 5

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Studies of the mechanism of radiation... S/190/61/003/006/005/019
B110/B216

shows that the addition of (~ 10 mole%) methyl methacrylate inhibits polymerization to a greater extent than the addition of isobutylene, but not as strongly as acrylonitrile addition. From this it is concluded that the inhibition increases with increasing electronegativity of the substituent at the double bond of the added monomer. There are 6 figures, 2 tables, and 10 references: 5 Soviet-bloc and 5 non-Soviet-bloc. The three references to English-language publications read as follows:
Ref. 3: R. Worrall, A. Charlesby, Journ. Appl. and Isot., 4, 84, 1958;
Ref. 5: W. J. Burlant, D. H. Green, J. Polymer Sci., 31, 227, 1958;
Ref. 7: A. Shapiro, V. Stannett, J. Chim. Phys., 56, 830, 1959.

ASSOCIATION: Nauchno-issledovatel'skiy fiziko-khimicheskiy institut im. L. Ya. Karpova (Scientific Research Institute imeni L. Ya. Karpov)

SUBMITTED: July 21, 1960

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25264 S/190/61/003/007/008/021
B101/B220

AUTHORS: Gromov, V. F., Khomikovskiy, P. M., Abkin, A. D.

TITLE: Copolymerization of acryl nitrile and ethylene under the effect of gamma radiation

PERIODICAL: Vysokomolekulyarnyye soyedineniya, v. 3, no. 7, 1961 1015 - 1019

TEXT: The copolymerization of ethylene with acryl nitrile (AN) under the effect of gamma radiation of Co^{60}, 20,000 g-equ radium, is studied. The tests were performed at 200C in solution of toluene, the pressure of the ethylene being 10 to 45 kg/cm^2 and the intensity of the dose 30 rad/sec. The ethylene obtained from ethanol contained the following impurities (in vol%): 0.05 propylene, 0.02 butylenes, 0.3 saturated hydrocarbons, 0.14 CO_2, 0.01 O_2. The AN had a boiling point amounting to 77.5 - 78.5°C. The polymerization was effected in steel ampullae with magnetic mixer. The ampullae were filled with AN dissolved in toluene, liberated from air by freezing and thawing in vacuum, and saturated with

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Copolymerization of acryl.... 25264 S/190/61/003/007/008/021
B101/B220

ethylene under the above-mentioned pressure. The polymer suspensions obtained were rinsed with methanol, dried in vacuum, and then their content in nitrogen as well as their viscosity in dimethyl formamide at 26°C and with a concentration of the polymer of 0.35 to 0.75 g/dl. were determined. Data obtained: 1) for molar ratios of ethylene: AN = 0.1:0.9 and 0.5:0.5 the yield of polymer is linearly dependent on the time of polymerization required to achieve a 40% conversion. For a ratio of 0.7:0.3 the rate of polymerization increases up to 25% conversion and then decreases; 2) the intrinsic viscosity of the polymers increases with the degree of conversion; 3) with long radiation (about 20 hr and more) and a molar part of the AN > 0.5 the polymers become insoluble due to cross linking; 4) the rate of polymerization increases with increasing concentration of the AN; 5) for all ratios the polymer contains relatively more AN than the initial mixture. In the range of concentrations of the AN from 0.1 - 1.0 molar parts, the equation $y = 0.718 + 0.046x + 0.0019x^2$ holds, wherein x is the content of AN in the initial mixture and y the content of AN in the polymer; 6) the calculated constants of copolymerization are: $r_{1(AN)} = 7$, $r_2 \approx 0$. r_1 de-

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creases, however, if the content in AN exceeds 0.7 molar parts; 7) the following constants were calculated for the copolymerization of ethylene with CO, based on the data given by M. Brubaker et al. (see below): $r_{2(CO)} = 0.25$; $r_{2(C_2H_4)} = 0.57$. G. S. Kolesnikov, A. P. Sunrun, and T. A. Soboleva are mentioned. There are 7 figures, 2 tables and 10 references: 5 Soviet-bloc, and 5 non Soviet-bloc. The most important references to English-language publications read as follows: M. Brubaker, D. Coffman, H. Hoehn, J. Amer. Chem. Soc. 74, 1509, 1952; W. Kay, Industr. and Engng. Chem. 40, 1459, 1948.

ASSOCIATION: Fiziko-khimicheskiy institut im. L. Ya. Karpova (Physico-chemical Institute im. L. Ya. Karpov)

SUBMITTED: September 20, 1960

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S/190/61/003/008/005/019
B110/B220

AUTHORS: Abkin, A. D., Sheynker, A. P., Yakovleva, M. K.

TITLE: Study of the mechanism of radiation polymerization. III. Mechanism of carbonium radiation polymerization

PERIODICAL: Vysokomolekulyarnyye soyedineniya, v. 3, no. 8, 1961, 1135-1139

TEXT: Previously, the authors had studied the effect of gamma radiation on polymerization and copolymerization of isobutylene, styrene, and methyl methycrylate (MMA) dissolved in ethyl chloride and shown that they proceed at low temperatures (-78°C) according to the carbonium mechanism (Mezhdunarodnyy sympozium po makromolekulyarnoy khimii, SSSR, Moskva (International Symposium of Macromulecular Chemistry, USSR, Moscow) June 14-18, 1960; Vysokomolek. soyed. 3, 716, 1961; ibid., 3 828, 1961). Some ideas with regard to this mechanism are put forward in the present paper. The initiation of polymer chains is effected by interaction between a monomer molecule and a proton presumably originating from the solvent. The following experimental data are given in confirmation of this assumption:

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Study of the mechanism of ...

1) The polymerization rate is a linear function of the monomer concentration; 2) radiolysis of ethyl chloride at 78°C yields a product closely related to dichlorobutene as to molecular weight (132) and refractive index (n_D^{20}=1.4812); 3) at -78°C the polymerization rate of isobutylene "in mass" ($46.7 \cdot 10^{-6}$ mole/l·sec) is lower than in a solution of ethyl chloride (concentration of isobutylene 12.6 mole/l: $71.2 \cdot 10^{-6}$ mole/l·sec). The following mechanism is assumed: The growing carbonium ion ejects a proton which forms a free radical with the negative molecular ion (counter-ion) of the monomer. The participation of the negative monomer ion is proved by the fact that the polymerization is strongly inhibited in the presence of a monomer with electron-acceptor properties. The copolymerization of isobutylene and styrene as well as of styrene and MMA follows the equation: $\omega = \left[(\lambda + 1)(r_1A^2 + 2AB + r_2B^2) \cdot \omega_a \omega_b\right] / \left[\lambda \omega_b r_1 A^2 + \chi \omega_a \omega_b AB + \omega_a r_2 B^2\right]$, where ω is the total rate of copolymerization; A and B are the concentrations of the monomers A and B, respectively; ω_a and ω_b are the rates of separate

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Study of the mechanism of ...

polymerizatio. of A and B, respectively; $\lambda = v_a/v_b$ is the ratio of the formation rates of active centers of A and B; $\chi = (k_{brA+B}/k_{incrA+B} + k_{brB+A}/k_{incrB+A})/v_b$, where k_{incr} = rate of chain growth; k_{br} is the rate of chain rupture. The two unknowns λ and χ can be determined experimentally from ω_a, ω_b, and from the copolymerization rates at different ratios of the monomers. Data obtained for the copolymers of isobutylene (A) and styrene (B): $\lambda = 4$; $\chi = 8 \cdot 10^6$; for styrene (A) and MMA (B) $\lambda = 10$; $\chi = 440 \cdot 10^6$. It was observed that the polymerization rate of styrene increased at -78°C with increasing surface of the reaction vessel. The authors established an effect that is analogous to that of solid admixtures observed by R. Worrall et al. (J. Appl. Rad. a. Isot., 4, 84, 1958). The monomer molecules adsorbed on the surface of the reaction vessel have a higher electron affinity than the molecules in the volume, and are able to capture secondary electrons. Thus, the lifetime of the carbonium ions effecting the polymerization process is prolonged. Moreover, the influence of the surface is confirmed by a reduction of the molecular weight of the

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polymer at -78°C when steel ampullae are used instead of glass ampullae. S. S. Medvedev is thanked for his interest. There are 2 figures and 7 references: 4 Soviet and 3 non-Soviet. The most important references to English-language publications read as follows: Ref. 4: A. Shapiro, V. Stannett, J. Chim. Phys., 56, 830, 1959. Ref. 6: F. R. Mayo, Ch. Walling, Chem. Revs., 46, 191, 1950. Ref. 7: R. Worrall, S. H. Pinner, J. Polymer Sci., 34, 229, 1959.

ASSOCIATION: Fiziko-khimicheskiy institut im. L. Ya. Karpova (Physico-chemical Institute imeni L. Ya. Karpov)

SUBMITTED: September 5, 1960

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1572, 1436, 1474

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S/190/61/003/011/013/016
B110/B147

AUTHORS: Unhakov, V. D., Mezhirova, L. P., Galata, L. A., Kostyuk, A. G., Khusnutdinova, Z. S., Medvedev, S. S., Abkin, A. D., Khomikovskiy, P. M.

TITLE: Polymerization of styrene and butadiene with styrene in emulsions under the action of initiating redox systems. I. Effect of the nature of peroxide compounds on the rate of polymerization

PERIODICAL: Vysokomolekulyarnyye soyedineniya, v. 3, no. 11, 1961, 1716-1722

TEXT: Aim of the present work was the determination of the most active initiating redox systems for the polymerization of butadiene with styrene in emulsions, and especially of the effect of the nature of peroxides on the rate of polymerization. Nekal with 20 % of Na_2SO_4 and NaCl and mersolate (mixture of Na salts of sulfonic acids of the aliphatic series: $C_{15}H_{31}SO_3Na$) with ≤ 5 % of NaCl served as emulsifiers. Peroxides were used

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Polymerization of styrene and...

as oxidants (Table). Potassium ferrocyanide and ferrous pyrophosphate complex (IV) served as reducing agents. The rate of polymerization was determined either dilatometrically or from the yield of polymer (in ampuls). Polymerization took place at 5°C with an excess of butadiene, styrene with peroxides dissolved in it (10 % solution), and the calculated amount of emulsifier solution. A suspension of the ferrous pyrophosphate complex was added at a certain temperature by means of medical syringes. Substances used: (1) mersolate (3 % by weight added to water, ratio monomer : emulsifier 1 : 1); (2) potassium ferrocyanide. The temperature was varied between C and 60°C. Seven peroxides were investigated in amounts equivalent to 0.02 and 0.1 % by weight of isopropyl benzene hydroperoxide. $K_4Fe(CN)_6$ was used in concentrations equimolecular to hydroperoxide. p-tert-butyl isopropyl benzene hydroperoxide (I) had the optimum rate of polymerization; that of ethyl isopropyl benzene peroxide, isopropyl benzene- (II), and ethyl benzene hydroperoxide was lower, that of dibenzyl hydroperoxide still lower, and that of benzoyl peroxide the lowest. Polymerization with H_2O_2 proceeds fast at the beginning, then it decreases strongly, since H_2O_2 and the reducing agent are readily soluble in water. With 0.2-0.5 % by weight

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of II, only the initial rate increases. The total yield is lower than with 0.1 % by weight of II. Between 0.75 and 1 % by weight of II, initial rates and total yield are much lower. With 0.02-0.2 % by weight of I, initial rates increase. Since the total rate decreases at 0.2 % by weight, the dependence of the reaction rate on the hydroperoxide concentration is probably linked with the inhibiting effect of the decomposition products of hydroperoxide. With 0.1 % by weight of I and an equimolecular amount of $K_4Fe(CN)_6$, both total yield and initial rate increased with increasing temperature. The activation energies were determined according to the Arrhenius equation and found to be: E = 8.6 kcal/mole for II and E = 5.7 kcal/mole for I. Reduction of E by 3 kcal/mole at ~ 0°C corresponds to a 200-fold increase of the reaction rate. Since the rate is twice as high at 0°C, the pre-exponential factor in the Arrhenius equation increases by 10^2 times with decreasing activation energy of I. For the copolymerization of butadiene with styrene (ratio 70 : 30) at 5°C, the following was used: Nekal (2.8 and 1.4 % by weight added to water), 0.44 % by weight of ferropyrophosphate (related to iron sulfate) of the monomer. The ratio organic phase : aqueous phase was 1 : 4 (by weight). In the case of 0.34 %

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by weight of hydroperoxide of II (equimolar ratio to the monomer) optimum rate was achieved with IV. The highest yield was achieved with aryl-alkyl hydroperoxides (I and 1,1-diphenyl ethane hydroperoxide (III)) (Table). With an emulsifier concentration of 2.8 %, maximum conversion (70-75 %) was achieved after 2 hr with 0.2 % by weight of I and with 0.3 % by weight of III. With 0.34 % by weight of II, optimum conversion (~30 %) was achieved after 2 hr. Polymerization of I and IV with 1.4 or 2.8 % by weight of emulsifier was constant up to 30 % conversion, then the rate dropped. With 1.4 % by weight, the initial rate was lower and the decrease more distinct. With an addition of 0.1 % by weight of hydroperoxide + 0.26 % by weight of IV (after 1 hr new addition of 0.1 % by weight of hydroperoxide and 0.18 % by weight of IV), constant polymerization took place up to 60 % conversion. Thus, the consumption of the initiating system causes a decrease in rate. The efficiency of redox systems and initiators depends on the reactivity of the radical as well as on the solubility of the peroxide compounds in the aqueous phase and in the monomers. The lower the solubility in water, the lower the loss and the stronger the initiating action. I + IV cause a higher rate of reaction than II + IV due to lower activation energy and lower solubility in water. For II + IV, the redox reaction occurs at the

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11.2211

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B110/B147

AUTHORS: Ushakov, V. D., Mezhirova, L. P., Galata, L. A., Khusnutdinova, Z. S., Sheynker, A. P., Medvedev, S. S., Abkin, A. D., Khomikovskiy, P. M.

TITLE: Polymerization of styrene and butadiene with styrene in emulsions under the action of initiating redox systems. IL Effect of the nature of the reducing agent on the rate of polymerization

PERIODICAL: Vysokomolekulyarnyye soyedineniya, v. 3, no. 11, 1961, 1725-1729

TEXT: The effect of the reducing component of initiating systems and of the addition of a second reducing agent on the rate of polymerization is studied. Used were systems of hydroperoxides (HP) of isopropyl benzene (I) or p-tert-butyl isopropyl benzene (II) with ferropyrophosphate complex (III), potassium ferrocyanide (IV), ferrous sulfate with o-phenantnroline, or of complexes of α,α-dipyridyl with ferrous oxalate. Sodium bisulfite and the bisulfite compound of acetone served as reducing

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is achieved after 4 hr at a ratio 0.5 IV : 1 HP. The high rate of polymerization for systems with III is caused by the low solubility of III in water. The redox potential of III is +200 mv. In dissolved state, it reacts with Fe^{2+}, but dissolves only slowly. This causes the great width of conversion. IV with high positive potential (420 mv) is soluble in water. The rate of initiating is determined by interaction of HP with IV. Polymerization is not initiated during the unproductive reaction of III soluble $NaHSO_3$ and well soluble HP I. $NaHSO_3$ and poorly soluble HP II initiate polymerization. The effect of IV on III at 20°C consists in the regeneration of the Fe^{2+} ions from the Fe^{3+} ions, thereby the width of conversion increases. As we are [illegible] figure [illegible] we will [illegible] references to [illegible] Ellis F. [illegible] Hill, T. Svoboda, J. Amer. Chem. Soc., 1, 43; [illegible] Kopling, Industr. and Engng Chem., 37, 299, [illegible]

[illegible] Institute [illegible]

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AID Nr. 993-6 19 June

RADIATION POLYMERIZATION OF TETRAFLUCROETHYLENE IN THE SOLID STATE (USSR)

Bruk, M. A., A. D. Abkin, and P. M. Khomikovskiy. IN: Akademiya nauk SSSR. Doklady, v. 149, no. 6, 21 Apr 1961, 1322-1325.

S/020/63/149/006/014/027

The radiation polymerization of tetrafluoroethylene (TFE) in the solid state has been studied at the Physicochemical Institute imeni L. Yu. Karpov.. Specimens of pure TFE were frozen by immersion in liquid nitrogen and irradiated from a Co^{60} source with an activity of 60,000 g-equiv of Ra or from an electron accelerator with an energy of 1.5 Mev. The yield of the polymers was determined gravimetrically following fast defreezing of irradiated specimens. The EPR spectra were recroded with the use of P3-1301 type devices; the absolute concentrations of radicals were evaluated by comparison of the signal areas of the sample and of a standard with

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a known concentration of paramagnetic particles. It was shown that 1) the initial polymerization rate of TFE in the solid state increases with temperature, attains a maximum near the melting point, and drops sharply after melting; 2) the total activation energy of polymerization is 0.6 kcal/mol in the -196 to -155°C range and 1.6 kcal/mol at -155 to -131°C; 3) rapid annihilation of radicals takes place in the -180 to -140°C range and in the -80 to -50°C range; and 4) the character of the radical annihilation and changes in the EPR spectra observed at low temperatures suggest that these spectra are associated with the radical formed in the monomer, and the spectra observed at -150°C and above, to the radical in the polymer. Finally, it is assumed that the polymer radical has the structure

and is formed in the system as a result of the growth of the polymer chain.

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S/183/62/000/001/001/001
B110/B147

15.5560

AUTHORS: Dorokhina, I. S., Abkin, A. D., Klimenkov, V. S.

TITLE: Copolymers of acrylonitrile and vinyl acetate

PERIODICAL: Khimicheskiye volokna, no. 1, 1962, 49 - 54

TEXT: The composition of copolymers of acrylonitrile (I) and vinyl acetate (II) in (a) aqueous emulsions, and (b) homogeneous dimethyl formamide solutions (DMF) with peroxide initiators in different steps of polymerization was studied. The following values were found for a: monomer:H_2O = 1:3, emulsifier concentration = 3% by weight of the monomer, K_2SO_5 concentration = 0.3% by weight of the monomer, temperature = 50°C; the values for b were: concentration of monomers in DMF = 4 moles/liter, benzoyl peroxide concentration = 0.048 moles/liter, temperature = 50°C. Copolymerization was first investigated in 30 - 40 ml dilatometers for a conversion of 10 - 15%. The copolymer obtained from an aqueous emulsion was coagulated by a 10% aqueous NaCl solution, that obtained from DMF by a 60 - 70% DMF solution. In this case, the copolymers were extracted by benzene. Further copolymerization in

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aqueous emulsions was investigated in a 6 liter reaction vessel in N_2 atmosphere ($< 0.05\%$ O_2) in the presence of K_2SO_5. The authors determined: (1) the composition according to nitrogen content (Kjeldahl), (2) characteristic viscosity of 0.5% solutions of the copolymers in DMF, (3) their solubility (qualitatively), (4) density, (5) vitrification temperature according to V. A. Kargin et al. (Ref. 6: ZhFKh, 23, 630 (1949)). When the degree of conversion was low, copolymers of different characteristic viscosities were obtained. The lower η_{char} of the copolymers obtained in DMF solution are caused by chain transfer through the solvent. The dependence of η_{char} on the initial monomer composition is caused by different reactivities of monomers and radicals formed from them. This dependence is practically the same for copolymers from a DMF solution and from aqueous emulsion. For an arbitrary initial component ratio, the copolymer is always enriched with I. The copolymerization constants ($r_1 = 4.2$, $r_2 = 0.05$) obtained according to L. Gindin et al. (Ref. 8: ZhFKh, 21, 1269 (1947)) show that the rate of addition of I to its own and to a foreign radical is higher than that of II. Since with

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arbitrary initial monomer ratios I is faster consumed than II, only II polymerizes in many cases. Integral copolymer composition changes with the degree of transformation, with the content of I decreasing. Differential copolymer composition changes stronger than integral copolymer composition, with homopolymerization of II taking place when I is exhausted. The intramolecular distribution of chain links was calculated from the formulas for the distribution functions according to L. Gindin et al. (Ref. 11: DAN, SSSR, 56, 2, 177 (1947)). With a high content of I in the initial mixture, the macromolecules are made up of long links of I connected by 1 - 2 links of II. Copolymerization of I and II (initial molar fraction of I = 0.679) with 70% yield results in an equimolar ratio with an integral composition of ~80% M of I. Macromolecules of the copolymer (50:50) consist of successive sections of I and II with 1 - 10 links of each component. Solubility increases, and specific gravity and vitrification temperature decrease when the fraction of II is increased. The fraction of the copolymer enriched with II acts as a plasticizer in fiber production, and deteriorates the properties of the fiber (resistance to heat). There are 6 figures, 5 tables, and 12 references: 5 Soviet and 7 non-Soviet. The three most recent references to English-language publications read as

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Copolymers of acrylonitrile...

follows: F. R. Mayo et al., J. Am. Chem. Soc., 70, 1523 (1948); R. M. Fordyce et al., J. Am. Chem. Soc., 70, 2489 (1948); T. Alfrey et al., J. Polymer. Sci., 5, 719 (1950).

ASSOCIATION: VNIIV

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"APPROVED FOR RELEASE: 04/03/2001 CIA-RDP86-00513R000100130002-4

DYURNBAUM, V.S.; ABKIN, A.D.; KLIMENKOV, V.S.

Composition and intramolecular distribution of copolymers of acrylonitrile with butylvinylsulfonate and methacrylamide. Khim. volok. no.2:10-14 '62. (MIRA 15:4)

1. Vsesoyuznyy nauchno-issledovatel'skiy institut iskusstvennogo volokna.
(Acrylonitrile) (Sulfonic acids) (Methacrylamide)

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"APPROVED FOR RELEASE: 04/03/2001 CIA-RDP86-00513R000100130002-4

S/183/62/000/005/001/002
B101/B186

AUTHORS: Dorokhina, I. S., Klimenkov, V. S., Abkin, A. D.

TITLE: Production of fiber-forming copolymers from acrylonitrile and vinyl acetate

PERIODICAL: Khimicheskiye volokna; no. 5, 1962, 16 - 21

TEXT: This second paper on copolymerization of acrylonitrile (AN) with vinyl acetate (VA) describes laboratory and pilot plant experiments in N_2 atmosphere at 50°C aimed at the production of copolymer fibers containing 3 - 20% VA, and lists the properties of the fibers. Results: A copolymer of the ratio AN : VA = 90 : 10 was found to have optimum properties. Because of the higher reactivity of AN, this was added in successive doses during the process, together with the regulator and the emulsifier, so as to obtain copolymers of constant composition. The inhibiting effect of O_2 contained in N_2 was suppressed by 0.03 - 0.05% hydrosulfite. Since the reaction velocity strongly increases owing to the redox system formed, N_2 was used with a maximum of 0.5 - 0.8% O_2. The following optimum conditions were found experimentally: ratio monomers : H_2O = 1 : 3; ratio AN : VA in

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the initial mixture equalling 68 : 32; content of initiator (water-soluble peroxide) 0.7% of the monomer weight; emulsifier (MK (MK) or Sulfanole) 3.0%; regulator (Diproxid) 0.03%; duration of process 4 hrs, yield 70-78%. In the laboratory test, the fiber was spun from 14 - 16% solution of copolymer in dimethyl formamide. Oxidized hydrocarbons (C_{12} - C_{15}) were used for the precipitation bath (90-100°C), and triethylene glycol for the drawing bath (100°C). In the pilot plant test, spinning was performed through spinnerets with 4800 or 12,000 openings, following a procedure developed for polyacrylic fibers, in a 40-60% dimethyl formamide precipitation bath. The "nitron B (V)" fiber showed a breaking length of 25 - 30 km, an elongation after embossing of 20-25%, and a shrinkage in boiling water of 25-30%. Increased shrinkage occurred with increasing VA content, fiber with 20% VA was poorly heat-resistant. The vitrification temperature was 80-82°C for 10% VA, and 65-70°C for 20% VA, as against 85-90°C for pure nitron (polyacrylic fiber). The new fiber can be colored by basic or disperse colorants. Colorability increases with increasing VA content. A VA content of 10-12% is recommended for the production of staple fiber, a VA content of 20% for fur manufactured from man-made fibers. There are 3 figures and 4 tables.

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Production of fiber-forming...

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ASSOCIATION: VNIIV

SUBMITTED: August 26, 1961

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S/069/62/024/005/003/010
B107/B186

AUTHORS: Dorokhina, I. S., Abkin, A. D., Klimenkov, V. S.

TITLE: The part played by the distribution of monomers between the phases in the emulsion copolymerization of acrylonitrile and vinyl acetate

PERIODICAL: Kolloidnyy zhurnal, v. 24, no. 5, 1962, 549 - 553

TEXT: The distribution of monomeric acrylonitrile and of vinyl acetate between the hydrocarbon phase and the liquid phase was examined at 50°C, both with and without the addition of MK (MK) as emulsifier. A likely reaction mechanism of the polymerization is suggested. The distribution by volume was determined after shaking together a mixture of monomers and water for one hour. The initial proportion by weight was 3:1. The proportionate amounts of acrylonitrile and vinyl acetate were determined by refractometry, applying a correction for the solubility of the hydrocarbon phase in water. The results are collected in Table 1 and Table 2. The ratio of acrylonitrile to vinyl acetate in the hydrocarbon phase is seen to be only slightly displaced, whereas considerable deviations appear

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in the aqueous phase. The solubility of the monomers is slightly greater in soap solution than in water. Polymerization experiments carried out with different quantities of emulsifier indicated that the polymerizing reaction proceeds firstly in the soap micelle and later in the polymeric monomer particles. There are 4 figures and 2 tables.

ASSOCIATION: Vsesoyuznyy nauchno-issledovatel'skiy institut iskusstvennogo volokna, Moskva - Mytishchi (All-Union Scientific Research Institute for Synthetic Fibers, Moscow - Mytishchi)

SUBMITTED: August 12, 1961

Table 1. Legend: a - composition of initial monomer mixture (acrylonitrile-vinyl acetate); b - hydrocarbon phase; c - aqueous phase; d - solubility of monomers in water in %; e, k, m - mole%; f, l, n - wt.%; g, i - composition of monomeric mixture (acrylonitrile - vinyl acetate); h, j - quantity of monomers in % of initial quantities.

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The part played by the distribution...

Table 2. Legend: a - composition of initial monomer mixture (acrylonitrile - vinyl acetate); b - soap solution (1% MK); c - hydrocarbon phase in the presence of the emulsifier; d - solubility of monomers in %; e, h, l - mole%; f, i, m - wt.%; g, k - composition of the monomer mixture acrylonitrile - vinyl acetate; j, n - quantity of monomers in % of initial quantities; o - in 1% MK solution; p - in pure emulsifier.

(a) Состав исходной смеси мономеров (АН—ВА)		(b) Углеводородная фаза				(c) Водная фаза			(d) Растворимость мономеров в вод., %
(e) мол. %	(f) вес. %	n_D^{20}	(g) состав смеси мономеров (АН—ВА) (k) мол. %	(l) вес. %	(j) количество мономера, % от исходного	(m) состав смеси мономеров (АН—ВА) (n) мол. %	(p) вес. %	(o) количество мономера, % от исходного	
100—0	100—0	1,37281	100,0	100,0	71,5	100—0	100—0	28,5	8,78
82,5—17,5	74,5—25,5	1,37447	80—20	71,3—28,7	75,5	90—10	85—15	24,5	7,5
61,6—38,2	49,5—50,5	1,37630	57—43	45—55	77,7	73—27	63—37	22,3	8,9
34,6—65,4	24,6—75,4	1,37878	37,8—62,2	27—73	81,3	27—73	18—82	18,7	9,9
0—100	0—100	1,37741	0—100	0—100	80,1	0—100	0—100	19,9	8,53

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The part played by the distribution...

Состав исходной смеси мономеров АН—ВА		Раствор мыла (1% МК)			Углеводородная фаза в присутствии затравки			Растворимость мономера, %	
		Состав смеси мономеров АН—ВА		количество мономеров, % от исходного	Состав смеси мономеров АН—ВА		количество мономеров, % от исходного	в 1%-ном растворе мыла МК	в чистой затравке
мол. %	вес. %	мол. %	вес. %		мол. %	вес. %			
100—0	100—0	100—0	100—0	28,5	100—0	100—0	71,5	8,78	8,78
82,5—17,5	74,5—25,5	87,5—12,5	81,1—18,9	25,65	81—19	72,4—27,6	74,35	7,83	—
61,6—38,4	43,5—56,5	72,8—27,2	62,3—37,1	22,41	57,2—42,8	45,1—54,9	77,59	6,95	—
24,6—65,4	24,6—75,4	23,2—76,7	17,3—82,7	17,3	37,9—62,1	27,3—72,7	82,7	6,1	—
0—100	0—100	0—100	0—100	16,8	0—100	0—100	83,2	6,3	64,0

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S/190/63/005/003/016/024
B101/B203

AUTHORS: Dorokhina, I. S., Abkin, A. D., Klimenkov, V. S.

TITLE: Kinetics of copolymerization of acrylonitrile and vinyl acetate

PERIODICAL: Vysokomolekulyarnyye soyedineniya, v. 5, no. 3, 1963, 385-392

TEXT: To study the possibility of synthesizing fiber-forming copolymers, the kinetics of copolymerization of acrylonitrile (AN) and vinyl acetate (VA) was investigated in dimethyl formamide (DMF) and in aqueous emulsion. In DMF the concentration of components was 4 moles/liter and copolymerization was performed at 50°C with 0.048 moles/liter benzoyl peroxide. In aqueous emulsion the monomer : water ratio was 1 : 3 and potassium persulfate served as initiator. The following values were calculated from the equations developed in the thesis by Abkin (Fiziko-khim. in-t im. L. Ya. Karpova, M., 1951) for the reaction in DMF: $\lambda = 1$, $\theta = 40$, $r_1 = 4.2$, $r_2 = 0.05$, constant of cross termination $k_{tAB} = 8.78 \cdot 10^8$ liters/mole·sec, constant of the initiation rate $k_A = k_B' = 2.65 \cdot 10^{-8}$ liters/mole·sec. For copolymerization in the emulsion, the values were: $\lambda = 8$, $\theta = 170$, con-

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Kinetics of copolymerization of...

stants of the rate of growth k_{BB} = 1632, k_{AB} = 86, k_{AA} = 361, k_{BA} = 32,700, $k_{tAB} = 3.73 \cdot 10^{10}$, $k_A = 22.4 \cdot 10^{-7}$, $k'_B = 2.8 \cdot 10^{-7}$ liters/mole·sec. The index A refers to AN, the index B to VA. There are 3 figures and 2 tables.

ASSOCIATION: Vsesoyuznyy nauchno-issledovatel'skiy institut iskusstvennogo volokna (All-Union Scientific Research Institute of Synthetic Fibers)

SUBMITTED: August 26, 1961

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S/190/63/005/004/001/020
B101/B220

AUTHORS: Mezhirova, L. P., Smigasevich, Z., Sheynker, A. P., Abkin, A.D.

TITLE: Carbanion mechanism of gamma ray initiated polymerization

PERIODICAL: Vysokomolekulyarnyye soyedineniya, v. 5, no. 4, 1963, 473-478

TEXT: The Co^{60} gamma ray initiated polymerization of acrylonitrile (AN) and copolymerization of AN with styrene (St) and methyl methacrylate (MMA) are discussed. Results: (1) At -78°C the polymerization of AN initiated by gamma irradiation was successful in triethyl amine only, while at 0°C the electron donor or acceptor properties of the solvents (triethyl amine, ethyl chloride, acetonitrile or butyronitrile) had no effect on the polymerization. (2) When copolymerization of AN with St was initiated by gamma rays, copolymers enriched with AN formed at low temperatures, while at normal temperatures an azeotrope characteristic of the radical polymerization of these monomers was formed. (3) Copolymerization of AN with MMA, initiated by gamma rays, yielded in triethyl amine at -78°C a polymer enriched with AN, independently of the initial ratio of the monomers. $r_{AN} = 7.0$, $r_{MMA} = 0.05$, these values being close to those for catalytic

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anionic polymerization. (4) The kinetics differs from that of radical polymerization. MMA polymerizes more slowly ($0.04 \cdot 10^{-5}$ mole/l·sec) than AN ($0.96 \cdot 10^{-5}$ mole/l·sec). (5) These differences confirm the carbanion mechanism suggested by the authors for the polymerization and copolymerization of AN by gamma irradiation at low temperatures. There are 3 figures and 2 tables.

ASSOCIATION: Fiziko-khimicheskiy institut im. L. Ya. Karpova (Physicochemical Institute imeni L. Ya. Karpov)

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B/190/63/005/004/002/020
B101/B220

AUTHORS: Gerasimov, G. N., Abkin, A. D., Khomikovskiy, P. M.

TITLE: Mechanism of heterogeneous polymerization of ethylene under the effect of ionizing radiations

PERIODICAL: Vysokomolekulyarnyye soyedineniya, v. 5, no. 4, 1963, 479-486

TEXT: A method was developed for determining the diffusion coefficient of ethylene in polyethylene by plotting the desorption curve, after the polyethylene had been previously saturated under pressure (up to 200 atm) with ethylene. The desorption-induced change in weight of the polyethylene was measured. The diffusion coefficient was at 25°C ~3.5, at 38°C ~6.0, at 50°C ~9.0. The solubility of ethylene in polyethylene is proportional to its volatility, and with constant volatility independent of the temperature. With constant temperature, the diffusion coefficient is independent of the solubility of ethylene. The specific surface and the pore diameter of the polyethylene was determined with krypton by the method of A. Zettlemover, A. Chanda, E. Gambble (J. Amer. Chem. Soc., 72, 2752, 1950). The specific surface was dependent on the conditions of polymerization; it was (m^2/g):20.2 with a dose of 62 r/sec, 300 atm, 70°C, irradiation time 10 hr;
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33.2 at 141/r sec, 400 atm, 25°C, 6 hr; and 18.0 at 141 r/sec, 400 atm, 25°C, 12 hr. Assuming cylindrical pores their internal diameter r_o and wall thickness d are calculated: $r_o = 1.66 \cdot 10^{-5}$ cm, $d = 6.32 \cdot 10^{-6}$ - $1.69 \cdot 10^{-5}$ cm. Based on the cylindrical model and using the method of J. Cranc (Mathematics of Diffusion, Oxford Univ. Press, London, 1957), a rate of ethylene addition at the radicals inside the polymer of 23.2 g/l·sec was found, whereas the experimental data vary between 8.5 and 45.0 g/l·hr. This difference is explained by the fact that the concentration of the reactive radicals inside the polymer is less than 10^{-3} mole/l. From the proportionality between rate of polymerization and specific surface it is concluded that the reactive radicals are mainly at the surface of the polymer. There are 4 figures and 3 tables.

ASSOCIATION: Fiziko-khimicheskiy institut im. L. Ya. Karpova (Physico-chemical Institute imeni L. Ya. Karpov)

SUBMITTED: November 5, 1961

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"APPROVED FOR RELEASE: 04/03/2001 CIA-RDP86-00513R000100130002-4

BRUK, M.A.; ABKIN, A.D.; KHOMIKOVSKIY, P.M.

Radiation-induced polymerization of tetrafluoroethylene in the solid state. Dokl. AN SSSR 149 no.6:1322-1325 Ap '63. (MIRA 16:7)

1. Fiziko-khimicheskiy institut im. L.Ya.Karpova.
(Ethylene) (Polymerization)

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