

teriostatic properties and were resistant to aging under uv light. CPJR

3217r Copolymerization of divinyl adipate with methylacrylate studied by polarography. A. M. Shur, M. M. Filimonova, and B. F. Filimonov (Kishinevsk. Gos. Univ., Kishinev). *Vysokomol. Soedin., Ser. A* 9(10), 2193-7(1967)(Russ). In 0.05M Et₄NOH, as base electrolyte, divinyladipate (I) (M₁) is hydrolyzed to AcH. The height of the polarographic wave (λ) due to AcH is proportional to I concn. In 0.05M Et₄NOH, Me acrylate (II) (M₂) has a polarographic halfwave potential of -1.88 v.; λ height gradually decreases (Brdicka and Wiesner, CA 41: 5403d). However, in 0.05M Et₄Ni II has a const. λ , which depends only on II concn. This difference in polarographic behavior of I and II was used to develop a sensitive anal. procedure for their detn. in the presence of each other. Copolymn. of I and II in sealed glass ampuls at 60° was carried out as described earlier (CA 56: 10385h). Samples were withdrawn and their I and II contents were detd. by polarography of aliquots in 0.05M Et₄NOH (for I) and 0.05M Et₄Ni (for II). Kinetic curves were constructed and monomer reactivity ratios were found: $r_1 = 0.1 \pm 0.1$, $r_2 = 4 \pm 1$; on the basis of reactivity per double bond, $r_1' = 0.05 \pm 0.05$, $r_2' = 8 \pm 2$. CPJR

3218s Free-radical polymerization of ethylene. VII. Effect of pressure on copolymerization of ethylene with vinyl chloride. F. I. Duntov, A. L. Gol'denberg, M. A. Litvinova, and B. L. Erusalimskii. *Vysokomol. Soedin., Ser. A* 9(9), 1920-3(1967)(Russ); cf. CA 63: 10070b. The influence of the pressure on reaction rate and the monomer relative reactivities in the copolymn. of ethylene and vinyl chloride in the presence of azobisisobutyronitrile at 300-1500 atm. was studied. The study used 2 compns.: 13-17% and 43-61 mole % vinyl chloride. In both cases, the copolymn. rate increases with increasing pressure, and the increase is more pronounced at higher ethylene content. Curves showing the dependence of copolymn. rate on pressure and on compn. are given, and reactivity ratios are 0.16 and 1.85 for ethylene and vinyl chloride at 300 atm., and 0.2 and 1.85 at 1500 atm., resp. Ir spectra are given for the copolymers, and bands are present at 833, 770, 752, 726, and 722 cm.⁻¹. Approx. 20% -CH₂CHCl(CH₂)₂CHClCH₂- is present in the copolymer. BRJR

3219t The crystallization of ethyl- and methyl-branched copolymers of polyethylene from dilute solution. P. J. Holdsworth and A. Keller (Univ. Bristol, Engl.). *J. Polym. Sci., Part B* 5(8), 605-12(1967)(Eng). The morphology of crystals was studied for both ethylene-propylene (I) and ethylene-1-butene (II) copolymers grown from 0.1% soln. I contained 8.4 and 27.9 Me-branches/1000 C-atoms and II had 11 and 31.4 Et-branches/1000 C-atoms. Mats of the crystals were annealed and their crystallinity was detd. by heat of fusion. Varying lamellar thickness with appropriate crystn. and annealing conditions caused no tendency for the branches to be ejected from the lattice. Both I and II were crystd. as chain-folded lamellae, within which the branches were accommodated, producing less regular crystal habits and less perfect chain packing than for the homopolymer. When allowance was made for differences in m.p., the variations of lamellar thickness with crystn. and annealing temps. and with solvent followed the trends established for linear polyethylene. BZJN

3220m Polymerization in an electric field. Norio Ise (Kyoto Univ., Kyoto, Japan). *Kyoto Daigaku Nippon Kagaku Zasshi Kenkyusho Koenshu* 1966(23), 47-56(Japan). Styrene (I), α -methylstyrene (II), iso-Bu vinyl ether (III), or *p*-methoxystyrene (IV) was polyind. by I₂ in 1,2-Cl₂C₂H₄ in an elec. field to give the following results (monomer, R_{FE}/R_{FO} , and P_E/P_O given): I, 1.0, 1.0; II, 1.25; 1.05, III, 1.28, 1.04; IV, 1.34, 1.8; where R_{FE} and (or) P_E are polymerization rate and d.p., resp., in an elec. field (1 kv./cm.) and R_{FO} and P_O are polymn. rate and d.p., resp., under standard conditions. The elec. field did not affect the rate and degree of radical polymn. with Bz₂O₂ as catalyst. R_{FE}/R_{FO} is const. with varied elec. field. The author suggests that the initial step is formation of an ion pair of monomer and catalyst and that the ion pair is equilibrated with free ions. The mechanism is discussed. I. Tabushi

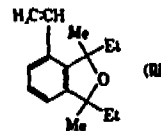
3221n Autocatalytic character of the thermal degradation of poly(vinyl chloride). L. S. Troitskaya, V. N. Myakov, B. B. Troitskii, and G. A. Razuvaev. *Vysokomol. Soedin., Ser. A* 9(10), 2119-25(1967)(Russ). Poly(vinyl chloride) thermal degradation dependence on pressure of HCl and the catalyst including org. acids, alcs., and phenols was studied. The HCl pressure at 179° and pressures of 60-665 mm. was studied, and the effect is given by the relation $dx/dt = dx_0/dt + kx^m p^n$ where dx/dt is the sum of the catalytic and noncatalytic rates, dx_0/dt is the rate of thermal degradation at 10⁻¹-10⁻² mm., p is the HCl pressure, x is the amt. of HCl, x_0 is the amt. of HCl at 10⁻¹-10⁻² mm., m and n are reaction order consts., and k is the reaction rate const. The consts. are given in the table. The uncatalyzed energy of activation for thermal degradation is 28 $\pm$ 1 kcal./mole, and the catalyzed energy of activation is 21 $\pm$ 1 kcal./mole. Curves showing the effect of org. acids at 180° including maleic anhydride, sebacic acid, ClCH₂CO₂H, stearic acid, lauric acid,

azelaic acid, crotonic acid, adipic acid, and succinic acid show 1 the acids accelerate the rate of degradation. Phenols stud

Temp.	Pressure, mm.	m	n	k
175°	60	1.4	0.9	9.1×10^{-4}
	105	1.4		
	655	1.4		
	465	1.5		
	75	1.4		
180°	145	1.5	0.9	1.1×10^{-4}
	145	1.5		
	418	1.5		
	645	1.4		
	55	1.4		
185°	105	1.6	0.9	1.5×10^{-4}
	310	1.5		
	505	1.5		
	65	1.5		
	205	1.4		
190°	385	1.5	0.9	2.0×10^{-4}
	570	1.5		
	570	1.5		

show that the accelerating rates decrease in the order phenol > 2,4-di-*tert*-butylphenol > 2,4,6-tri-*tert*-butylphenol. The mechanism of the degradation was studied. The HCl attacks vicin H and Cl to form double bonds and the alcs. and phenols attack labile Cl atoms. BRJR

3222p Styrene derivatives. VII. Polymerization of *o*-substituted 4-vinylphthalans. G. M. Pogosyan, A. A. Chokyan, Al'b. A. Saakyan, and S. G. Matsoyan. *Vysokomol. Soedin., Ser. B* 9(5), 365-8(1967)(Russ). 1,3-Dimethylvinylphthalan (I), 1,1,3,3-tetramethyl-4-vinylphthalan (II), 1,3-dimethyl-1,3-diethyl-4-vinylphthalan (III), and 1,3-bis(cyclo-



pentamethylene)-4-vinylphthalan (IV) were polyind. in bu or in a C₆H₆ soln. in the presence of Bz₂O₂ or azobisisobutyronitrile. The polymn. rate increased with initiator concn. at with an increase of temp. from 80 to 100°. All the polymers formed were powderlike and sol. After 2 hrs. polymn., *t*-yields were 13-19.5, 32-95, and 79-89% and the polymer softening temps. were 220-40, 300-20, and 270-95° for polymers of II, and III, resp. The yield of IV polymer (softening temp. 369°) was 68-82% within 9.5-32 hrs. Cf. CA 67: 11667g. BMJR

3223q Ultrasonic absorption in polymer solutions. Polystyrene in toluene. Hiroyasu Nomura and Yutaka Miyahara (Nagoya Univ., Nagoya, Japan). *Nippon Kagaku Zasshi* 88(5), 502-4(1967)(Japan). The ultrasonic absorption in soln. of polystyrene in toluene was measured by a pulse-echo method at 20 Mc./sec. In the plot of α/f^2 (α is the amplitude absorptivity coeff. and f the frequency) vs. polymer concn., a break point was observed which was shifted toward low concns. with increasing mol. wt. of the polystyrene. For concns. above the break point the α/f^2 vs. concn. curve was independent of the mol. wt. The break point was ascribed to the onset of entanglement in the polymer soln. Yutaka Miyahara

3224r Radiation-induced solid-state polymerization of butane diol dimethacrylate. I. G. Gusakovskaya and V. I. Gol'danskii. *Vysokomol. Soedin., Ser. B* 9(5), 390-2(1967)(Russ). Within the exptl. error range, butane diol dimethacrylate (I) did not polymerize at -196° under the effect of γ -irradn. This was observed to be independent of the freeing rate of I. When prior to the irradn., I was frozen at 1°/min., the monomer polyind. on subsequent melting in the m.p. region. At a cooling rate of 600°/min., the polymn. occurred in 2 temp. regions: at -107 to -85° (crystn. temp.) and at the m.p. BMJR

3225s Preparation and electrical properties of poly(tetracyanoethylene copper chelate) film. Tuneso Naraba, Yoshihiko Mizushima, Haruo Noake, Atsuo Nishioka, Yoshitaka Igarashi, Akira Imamura, and Yoshikazu Torihashi. *Rev. Elec. Commun. Lab. (Tokyo)* 15(7-8), 551-62(1967)(Eng.). Poly(tetracyanoethylene Cu chelate) films were prepd. by heating tetracyanoethylene and a Cu plate in a sealed, evacuated glass tube. The max. yield of chelate was obtained at 400°. Yield increase rapidly with reaction time up to about 30 min., and then increase more slowly. The yield during the second stage of the reaction was linearly dependent on the sq. root of the time. The film formed on plates pretreated by high-frequency heating was thinner than those formed on plates treated only by electro-polishing, but films were obtained even on plates with a surface oxide layer. The film contained 24-8 wt. % Cu. Electroprobe microanalysis showed the Cu concn. to be 30-6% at the base layer and 20% on the upper surface. The films showed *p*-type cond., with the activation energy for cond. varying from 0.1 to 0.5 ev. Resistivity showed a marked anisotropy, with space-charge-limited characteristics in the perpendicular direction. Heat treatment decreased the resistivity and space-charge cond. The dielec. const. and loss factor decreased with increasing frequency. Other metals with electronegativity <1.9 and