degrees range when heated in an evacuated capillary; some discoloration occurred in the 230–250° range when heated in air. The best sample obtained melted at 267–272° and probably had a molecular weight, $\bar{M}_n$, of about 20,000. The polymer was insoluble in boiling benzene and chlorobenzene, but dissolved in tetralin at 180° and did not immediately reprecipitate until cooled to 120°. The polymer recrystallized from tetralin solution showed high X-ray crystallinity, but not the needle-like particle form of the original polymer. The X-ray diffraction pattern showed "d" spacings of 7.2(w), 5.1(s), 4.2(s), 4.1(w) and 3.7(w). The infrared spectrum showed the complete absence of vinylene groups, indicating that the material was entirely a 1,4-addition polymer. The identity period of the polymer has been reported to be 4.35 Å.[10]

2,3-Dichlorobutadiene Polymer.—Except for one very low quality early specimen, all our samples of this polymer appeared to cross-link rather than melt on heating. The samples started darkening near 240° but did not melt below 300°. The polymer was insoluble in boiling benzene but dissolved readily in boiling chlorobenzene and in hot tetralin. The intrinsic viscosities observed suggest that the polymer was obtained in the same molecular weight range as the 2,3-dimethylbutadiene polymer.

By growing macroscopic needles of the thiourea–diene adduct (run 18) and converting these to polymer in the usual way, it was possible to obtain needle-like "crystals" of polymer which were 2–3 mm. long. X-Ray rotation patterns of these resembled typical fiber patterns, showing about 24 independent reflections arranged along the equator and two layer lines. In addition, there were very strong first and second order reflections on the meridian which lay just inside the layer lines. These reflections were missing from the powder patterns of polymer which had been recrystallized from solution, although the other reflections were sharpened by this treatment. It was concluded that in the needles of crude polymer, the polymer chains were all lined up parallel to the needle axis, but only partially ordered with respect to each other into crystallites. The chains in the disordered regions thus behaved as one-dimensional gratings with a repeating distance of 4.70 Å., giving the meridional reflections, while those in the ordered regions gave the normal diffraction pattern of a crystalline polymer with a 4.86-Å. identity period.

The infrared spectra of the polymers were free of any C=C stretching or vinylene H-wagging bands. This, along with the observed identity period, indicates that the polymer was entirely in the *trans*-1,4-configuration.

1,3-Cyclohexadiene Polymer.—Again, the properties of the crystalline polymer obtained from the canal complex polymerization contrasted sharply with those of the ordinary thermal polymer, which is a rubber.[13] The better samples melted at 370–380°. One sample was observed to be soluble in hot tetralin when freshly prepared, but otherwise all the samples contained some insoluble material. The infrared spectra indicated the presence of *cis* double bonds and were generally consistent with that expected for a substituted cyclohexene. The X-ray rotation pattern given by a single needle of the polymer showed three equatorial reflections, but none on layer lines or the meridian. The equatorial reflections had "d" spacings of 5.07(m), 4.42(m) and 4.04(s); upon repeating the photograph after standing for a month the last two reflections disappeared and the first became strong. Presumably, the chemical change which gave cross linking in the solid polymer was continuing.

It is difficult to see how any 1,3-cyclohexadiene polymer structure other than *trans*-1,4 could be formed in a thiourea canal or could give the observed interchain spacings. However, the *trans*-cyclohex-2-en-1,4-diyl repeating unit, unlike those of the acylic dienes, is pseudoasymmetric in the same sense as is that of a vinyl polymer, and hence should also be capable of the isotactic–syndyotactic–atactic type of stereoisomerism. The absence of meridional or layer line reflections provides suggestive, but not conclusive, evidence that the *trans*-1,4-poly-(1,3-cyclohexadiene) obtained was atactic. This, if true, would indicate that the cyclohexadiene polymerization in thiourea showed positional and geometrical specificity, but not stereospecificity.

Vinylidene Polymers.—The specimens of polyvinylidene chloride and polyisobutylene prepared by canal complex polymerization did not seem to differ from ordinary specimens of these polymers in appearance or infrared spectra, except that all of the polyvinylidene chloride specimens were quite brownish, even when only 1 Mr. was used for polymerization. The liquid polymer obtained in very small yield from 2-chloropropene was nearly colorless and gave an infrared spectrum indicative of a saturated hydrocarbon structure containing methyl and chloro groups. The polymer from 2-bromopropene was a dark yellow viscous liquid which turned black on standing overnight at room temperature.

Cyclohexadiene Oxide Polymer.—The monomer for this polymer, a liquid b. 50–55° (12 mm.), was prepared in poor yield by the perbenzoic acid oxidation of 1,3-cyclohexadiene[14]; it is reported to be the 1,4-endoxo compound 7-oxabicyclo[2.2.1]heptene-2. The tan solid polymer obtained (run 30, Table III) showed prominent infrared bands indicative of *cis*-olefinic and ether linkages. Thus, the polymer was probably a poly-(cyclohex-2-en-1,4-diyl) ether. This formation of a polyether by irradiating a cyclic ether is not unique; it has also been observed to occur when butadiene monoxide is irradiated in the solid state.[15]

Acknowledgments.—The authors wish to acknowledge the assistance of Mrs. Nancy R. Young in carrying out many of the experiments and thank Mr. J. S. Balwit for the irradiations, Miss M. O. Fragomeni and Miss D. V. McClung for the infrared spectra, and Mr. E. M. Hadsell and Mrs. M. M. Grenoble for the fractional distillations of the monomers used.

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[13] F. Hoffman and P. Damm, *Mitt. Schles. Kohlenforsch. Inst. Kaiser-Wilhelm Ges.*, **2**, 97 (1925); *C. A.*, **22**, 1249 (1928).

[14] M. Tiffeneau and B. Tchoubar, *Compt. rend.*, **212**, 581 (1941).

[15] W. G. Woods, private communication.

[CONTRIBUTION FROM THE GENERAL ELECTRIC RESEARCH LABORATORY, SCHENECTADY, N. Y.]

Stereospecific Polymerization in Urea Canal Complexes[1]

BY DWAIN M. WHITE

RECEIVED MAY 5, 1960

The possibility of preparing crystalline stereospecific polymers by irradiation of monomers in urea canal complexes was investigated. Polymers of 1,3-butadiene, vinyl chloride, acrylonitrile, acrolein and a mixture of vinyl chloride and acrylonitrile were prepared by this method in larger than trace quantities. The polymers of the first three monomers were crystalline and probably linear. Two which are of particular interest are the polybutadiene which was the all-*trans*-1,4-polymer and the polyvinyl chloride which was an insoluble crystalline solid.

The polymerization of olefins in thiourea canal complexes by ionizing radiation was described in the preceding paper.[2] This technique utilized the specific orientation and possible activation of the monomers by the complex to obtain highly regular

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[1] Presented in part before the division of Polymer Chemistry at the 134th Meeting of the American Chemical Society, Chicago, Ill., 1958, p. 2-T.

[2] J. F. Brown, Jr., and D. M. White, THIS JOURNAL, **82**, 5671 (1960).

polymers. Other reports describe polymerizations in canal complexes without initiation. 2,3-Dimethylbutadiene polymerized after a long standing at room temperature to a polymer[3] which was lower melting than the analogous product initiated by ionizing radiation.[2] Polymerization of 1,3-butadiene in the presence of urea with heat and pressure produced soft rubbery products.[4] The reaction conditions and the properties of the product indicate that the polymerization did not occur in the urea canals. The present paper reports the polymerization of 1,3 butadiene, acrylonitrile, vinyl chloride, acrolein and certain other monomers and mixtures of monomers in urea complexes at low temperatures, and describes the conditions required and the properties of the polymeric products.

The structure of the urea lattice in urea complexes is similar to the thiourea lattice except that the dimensions of the unit cell are smaller.[5,6] The most important effect of the change in lattice size with regard to polymerization is that the diameter of the canal is approximately 1 Å. less than in thiourea. This permits an entirely new class of monomer structures to be included and polymerized in the urea lattice. In general, these molecules are smaller and less branched than those which polymerize in thiourea. Several reports describe the variety of compounds that form complexes and the structural features which determine whether complex formation occurs.[2,3,7]

The Urea-Butadiene Complex.—An inclusion complex was reported by Clasen[3] to form when urea, 1,3 butadiene and a trace of methanol were combined at −80°. We have found that at −78° complex formation proceeded very slowly. At higher temperatures (approximately −55°) a stable complex formed within a week. Temperatures in this range were optimal since at higher temperatures (above −25°) the complex dissociated, and at −78° only poor yields of polymers were obtained. The formation of this complex, as indicated by polymerization upon subsequent irradiation, did not occur unless a trace of solvent was present. When no solvent was present the complex did not form. Small quantities of methanol (0.001 to 0.005 ml. per gram of urea) produced a maximum yield of polymer. When the quantity of solvent approached 0.1 ml. of methanol per gram of urea the yield of polymer dropped. With 0.33 ml. of methanol only a trace of polymer was detected. Ethanol was also an effective solvent. Acetone functioned poorly and produced a low yield of polymer.

Because of the low concentrations of methanol which are effective, we believe that the function of the methanol is not one of partially dissolving two species of dissimilar polarity but rather is to form a methanol-urea complex. This complex could then act as a seed to nucleate growth of the hexagonal urea lattice containing the monomer molecules.[8] When large quantities of solvent are present the sequence of monomer molecules in the canals is probably occasionally broken by solvent molecules. This would be expected to limit chain growth during polymerization. The same effect was noted when *n*-butane was added to the butadiene (*vide infra*).

The molar ratio of urea to butadiene in the complex was reported by Clasen to be 4.2.[3] It was observed, however, that a considerably larger proportion of butadiene was required to produce moderate yields of polymer (Table II). The increase in intrinsic viscosity and yield of the polymer with an excess of monomer can be explained by a displacement of the equilibrium

$$\text{monomer (free)} \rightleftarrows \text{monomer (complexed)}$$

to the right. The excess monomer would be expected to decrease the number of void areas in the canals. Such voids stop the chain propagation reaction as effectively as an impurity since the active chain end would be separated from the nearest monomer molecule.

Polymerization of Butadiene.—Butadiene in a urea complex polymerizes readily when irradiated with high energy electrons (Table III). Very low irradiation doses produced high molecular weight polymer but in low yields. As the dose increased the yield increased but the intrinsic viscosity and melting point of the polymer decreased. These observations are believed to indicate that monomer molecules in the longest uninterrupted canals are more likely to be polymerized than those in shorter canals. This is reasonable if one assumes that the number of active sites generated by low irradiation doses is insufficient to initiate polymerization in all canals, and that the same number of active sites is required to polymerize all of the monomer (or at least the same proportion of the monomer) in any canal regardless of the length, since the longer canals must occupy a greater area than the same number of small canals. Thus, the polymer from low irradiation doses does not represent an even distribution of polymer from all of the canals on a weight percentage basis but predominantly polymer from the longer canals. With higher irradiation doses, monomer in the remaining, primarily shorter, canals is polymerized too. This causes the molecular weight to be lower but the yield only slightly higher. There is a possibility that the higher doses may have caused chain scission and some grafting of urea to the polymer chain. Cross-linking is unlikely since each polymer chain is isolated from other chains by the urea lattice.

Polybutadiene Structure.—The data obtained support a 100% *trans*-1,4-polybutadiene structure. Titration of the ethylenic groups with iodine monobromide[9] indicated that the polymers contained 1.00 olefinic group for every four carbon atoms. Quantitative estimation of the intensity of the olefin absorptions in the infrared spectrum of the

(3) H. Clasen, *Z. Elektrochem.*, **60**, 982 (1956).

(4) British Patent 737,235, Sept. 21, 1955.

(5) A. E. Smith, *Acta Cryst.*, **5**, 224 (1952).

(6) H. U. Lenné, *ibid.*, **7**, 1 (1954).

(7) W. Schlenck, *Ann.*, **565**, 204 (1949); **573**, 142 (1951); O. Redlich, *et al.*, THIS JOURNAL, **72**, 4161 (1950); R. W. Schiessler and D. Flitter, *ibid.*, **74**, 1720 (1952).

(8) (a) A similar function for solvent was suggested for acetone with urea complexes by R. Rigamonti and M. Panetti (Abstracts for the Meeting of the International Union of Pure and Applied Chemistry, 1957, p. 50). (b) The interaction of solid urea and methanol has been described previously [see, *e.g.*, N. Yada and K. Matsuda, *J. Chem. Soc. Japan, Ind. Chem. Section*, **59**, 181 (1956); *C. A.*, **51**, 10040 (1957)].

(9) S. Siggia, "Qualitative Organic Analysis *via* Functional Groups," Second Edition, J. Wiley and Sons, Inc., New York, N. Y., 1954, p. 72.

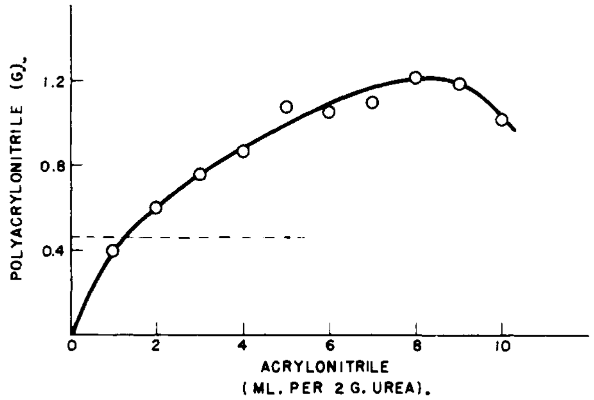

Fig. 1.—Plot of yield of polyacrylonitrile as a function of acrylonitrile complexed with 2.0 g. of urea. Dashed line represents theoretical yield of polymer for a packing of one monomer molecule per 7.1 Å. of canal.

polybutadiene indicated that at least 99% of the butadiene units contained *trans* disubstituted double bonds. No other types of unsaturation were detected. The infrared spectrum was similar to the spectrum for *trans*-polybutadiene published by Short[10] except for an additional band of medium intensity at 12.95 μ in the canal complex polymer. Recently the 12.95 μ band has been reported to be due to crystallinity.[11] Further structural evidence was obtained from the X-ray pattern. Powder diagrams of the polymer after the urea had been removed by extraction with acetone displayed seven rings. The most intense ring had a "d" spacing of 3.95 Å. Recrystallization of the polymer from benzene gave a sharper pattern of twenty-eight rings with the most intense corresponding to 3.94 Å. The pattern appears to be the same as that reported by Natta for *trans*-1,4-polybutadiene.[12]

The melting point of *trans*-1,4-polybutadiene from heterogeneous polymerizations is reported to be 135°.[12] Unrecrystallized polybutadiene samples prepared in urea complexes had melting ranges up to 147—154°. Before recrystallization from benzene the melting ranges of the acetone extracted polymers could be correlated with their intrinsic viscosities. The low viscosity samples had lower melting ranges. After recrystallization from benzene the polymers had melting ranges of approximately 135-137°.

The X-ray and melting point data indicate that the unrecrystallized *trans*-1,4-polybutadiene obtained from the urea complex had a crystal structure different from that of polymer samples which had been crystallized from solution. This difference is believed to be due to the orientation afforded by the canal. When the urea is extracted from the irradiated complex, the polymer retains at least part of the configuration it had in the canal, and would not be expected to form any crystal structure involving folded chains.

The observed polymer structure and the reported complexing ratio raise an interesting question regarding the polymerization mechanism. The reported[3] ratio of 4.2 urea molecules per butadiene implies that 7.7 Å. of canal length is occupied per monomeric butadiene molecule. The $—CH_2—CH═CH—CH_2—$ unit in the polymer, however, is only 4.9 Å. long. Thus, toward the end of the polymerization reaction it would seem necessary for the monomer molecules to move through several thousand ångström units along the canal in order to join the active end group. It is possible, of course, that the reported complexing ratio, which is a difficult quantity to measure accurately, may have been in error and a closer packing of monomer molecules does occur.

The yields and intrinsic viscosities of the polymers were lowered by the incorporation of *n*-butane in the butadiene–urea complex (Table IV). This effect is similar to the effect of traces of 2,3-dimethylbutane in the polymerization of 2,3-dimethyl-1,3-butadiene in a thiourea complex.[2]

Preparation and Irradiation of the Acrylonitrile–Urea Complex.—The presence of a trace amount of solvent was not essential for the formation of the acrylonitrile–urea complex, in contrast to the solvent requirements for preparation of the butadiene–urea complex. Small quantities of methanol did not appreciably increase the polymer yield while a large quantity prevented polymer formation (Table V). Since methanol complexes with urea at low temperatures,[8b] the formation of the methanol–urea complex may have depleted the supply of urea for the formation of the acrylonitrile–urea complex. Complex formation occurred readily at −78°. The complex, prepared at −55°, dissociated when the temperature was raised to −20°; at −25° the complex did not form.

The quantity of acrylonitrile used had a marked effect on the quantity of polymer produced after irradiation (Fig. 1). A moderate excess of monomer afforded an increased yield and higher intrinsic viscosity for the polymer. The reduction in yield when a large excess of acrylonitrile was added may have been due to absorption of radiation by the excess monomer to lower the effective dose the complex received. Although the yield of polymer was decreased, the intrinsic viscosity remained unchanged. The dashed line in Fig. 1 represents the maximum yield of polymer that would result from polymerization of monomer molecules packed end to end in the canal. The observed maximum yield of 1.22 g. of polymer corresponds to one molecule of acrylonitrile per 2.7 Å. of canal. This requires the molecules to be packed flat against each other if a normal canal complex is involved.

From measurements on Courtauld models the dimensions of the acrylonitrile molecule are approximately 7.1 Å. long, 4.7 Å. wide and 3.5 Å. thick. The thickness of 3.5 Å. is partially due to the π-electron clouds which would have to be distorted to permit the molecules to pack into 2.7 Å. lengths of canal. The diameter of the canal in the hexagonal urea lattice from electron density projections[5] varies from 5 to 6 Å. If there are some interstitial spaces between the molecules comprising the canal

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(10) J. N. Short, V. Thornton and G. Kraus, *Rubber Chem. and Tech.*, **30**, 1118 (1957). The 11.0 μ band, due to small amounts of 1,2-additions in the heterogeneous polymerization, was absent in the canal-type polymer.

(11) V. N. Nikitin, *et al.*, *High Mol. Wt. Compds.*, **1**, 1094 (1959).

(12) G. Natta, P. Corradini and L. Porri, *Atti. accad. naz. Lincei, Rend. Classe sci. fis. mat. e nat.*, **20**, 728 (1956).

wall or if there is some deformation of the wall, the flat packing may be possible.

Since even the most efficient packing without π-orbital deformation does not account for all of the polymer that is obtained, it is possible that either there is some polymerization outside of the canals or a complex other than a canal complex is formed. Polymerization of uncomplexed monomer is not important since at $-78°$ irradiation of pure acrylonitrile or an uncomplexed mixture of acrylonitrile and urea produced only traces of polymer.

Formation of some non-canal complex was indicated by the formation of a fluffy solid product when 10 ml. of acrylonitrile was mixed with 2 g. of urea. Larger quantities of monomer were not absorbed. Two-thirds mole of acrylonitrile was polymerized per mole of urea although the molar ratio of acrylonitrile to urea was four to one. If non-canal type complexing took place in addition to canal complexing, the polymerization may have occurred in both systems.

Another possibility is that the polymerization of free monomer adsorbed on the surface of canal complex crystals may be initiated by active chain ends projecting from canals. This possibility seems unlikely since polymerization of uncomplexed acrylonitrile in the presence of urea did not occur appreciably at $-78°$. Furthermore, polymerization of acrylonitrile in a urea complex immersed in chloroprene (which does not complex with urea) produced a polymer, although in lower yield, that did not contain any chloroprene units.

Polyacrylonitrile Structure.—The polyacrylonitrile isolated by trituration of the irradiated complex with aqueous acetone at 25° absorbed in the infrared at 4.95, 5.94 and 6.20 μ. Three additional triturations reduced the bands at 5.94 and 6.20 μ but produced a new band at 5.86 μ. Continuous extraction with boiling water removed the 4.95 and 5.86 μ bands and left only a weak 5.94 μ band. The 5.94 and 6.20 μ bands probably were due to traces of urea and water. The 4.95 μ band was probably due to a ketene-imine group[13] which hydrolyzed later during the extraction with hot water. The development of the 5.86 μ band and its disappearance may have been due to an intermediate in the hydrolysis of grafted urea side chains.

The infrared spectrum of the water-extracted polymer was similar to commercial polyacrylonitrile although minor differences were noted. The urea complex polyacrylonitrile did not have the absorption bands of the commercial polymer at 5.75, 6.14, 7.62 and 9.63 μ. Furthermore, the canal type polymer had more intense bands at 8.16 and 8.5 μ and the new weak band at 5.94 μ. The behavior of the polymer upon heating and its solubility in organic solvents were identical to commercial polyacrylonitrile.

The X-ray powder diagram of canal-type polyacrylonitrile contained three rings with "d spacings" of 5.3 (strong), 3.0 (weak) and 2.1 Å. (very weak). A sample of commercial polymer displayed rings at 5.3 (strong), 4.2 (medium) and 3.0 Å. (weak). The X-ray and infrared data indicate that the canal-type polyacrylonitrile does differ from the normal polymer. The differences, which are not large, may be a result of the orientation of the polymer imposed by the urea canal. The orientation persists even after removal of the urea.

Preparation and Irradiation of the Vinyl Chloride-Urea Complex.—Vinyl chloride formed a fluffy white complex with urea. The factors influencing the yield of polymer were similar to those for the butadiene-urea system although the yields were lower. With a small amount of solvent such as methanol the complex formed in several days at $-55°$. A 20 to 50% excess of monomer (based on close packing of vinyl chloride in the canals) gave the highest yields of polymer. The yield of polymer increased with the quantity of irradiation although only slightly with doses over 5 Mr.

Polyvinyl Chloride Structure.—Irradiation of the vinyl chloride-urea complex at $-78°$ produced a white insoluble solid polymer. When heated, the polymer began to darken at 150° as hydrogen chloride evolved. The brown solid residue did not fuse even at 400°.

The infrared spectrum of the polymer was similar to that of normal polyvinyl chloride[14] but there were significant differences. The absorption bands of the canal-type polymer were sharper than those of the normal polymer. The canal-type polymer exhibited weak bands not present in normal polymer at 2.95, 5.7 to 6.0 and 16.7 μ while normal polymer had medium bands at 14.4 and 16.3 μ that were not present in canal-type polymer. The spectral pattern in the 16–17 μ region is believed[14] to indicate that the canal-type polymer possessed a highly stereoregular structure.

The location and intensity of absorption bands in the carbonyl region varied with the method of isolation and purification of the polymer. Extensive solvent extraction reduced the absorption at 5.9 μ and increased the absorption at 5.77 μ. It has been suggested that the removal of remaining traces of urea was accompanied by oxidation of the polymer chain to form ketonic groups.[15]

An X-ray powder diagram of canal-type polyvinyl chloride displayed six rings with "d spacings" of 2.2 (weak), 2.5 (weak), 2.9 (diffuse), 3.5 (strong), 4.7 (medium), and 5.2 Å. (medium). This pattern for canal-type polyvinyl chloride was also observed by Sakurada and Nambu[16] and fits calculated values for syndiotactic polyvinyl chloride given by Natta and Corradini.[17]

Canal-polymerized vinyl chloride was not soluble in common solvents (aromatic and aliphatic halides, hydrocarbons, ketones, esters, sulfones, sulfoxides and amides) nor did it swell in them. To reduce the

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[13] Ketene-imine groups have been detected in polymethacrylonitrile prepared by free radical initiation. In the case of polyacrylonitrile, however, the group was not detected. M. Talat-Erben and S. Bywater, *Simposio internazionale di chimica macromoleculare, Suppl. a La Ricerca Sci.*, **25**, 1 (1955).

[14] S. Krimm, *Plastics Engineers J.*, **15**, 797 (1959); S. Krimm, *et al.*, *Chemistry & Industry*, 1512 (1958); R. J. Grisenthwaite and R. F. Hunter, *ibid.*, **719**, 1513 (1958); S. Narita, *et al.*, *J. Polymer Sci.*, **37**, 273, 281 (1959); T. Shimanouchi, *et al.*, *J. Chem. Phys.*, **30**, 1365 (1959).

[15] M. Goodman, private communication.

[16] I. Sakurada and K. Nambu, *J. Chem. Soc., Japan*, **80**, 307 (1959).

[17] G. Natta and P. Corradini, *J. Polymer Sci.*, **20**, 251 (1956).

TABLE I

EFFECT OF SOLVENT AND TEMPERATURE ON THE POLYMERIZATION OF 1.3-BUTADIENE

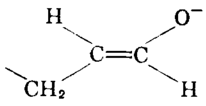
Sample	Butadiene, g.	Urea, g.	Solvent,[a] ml.	Temp. of complex formation, °C.	Time for complex formation, days	Irradiation dose, Mr.	Polymer weight, g.	M.p. range, °C.	Intrinsic viscosity,[b] dl./g.
1	1.50	1.00	0	−55 to −78	7	1	Trace		
2	0.80^c	1.00	M, 0.001	−55	11	1	0.224		1.62
3	$.80^c$	1.00	M, .005	−55	11	1	.223		1.62
4	$.80^c$	1.00	M, .010	−55	11	1	.182		
5	$.80^c$	1.00	M, .050	−55	11	1	.180		
6	$.80^c$	1.00	M, .10	−55	11	1	.135		1.23
7	3.0	3.0	M, 1.0	−50 to −78	6	2	Trace		
8	3.0	3.0	M, 0.1	−50 to −78	6	2	0.37		
9	1.5^c	1.5	M, .04	−55 to −78	7	1	.204		0.93
10	2.0	2.0	M, .03 W, .03	−78	11	2	.03	130–140	
11	2.0	2.0	M, .03 W, .03	−50	11	2	.29	134–138	.60
12	2.0	2.0	M, .03 W, .01	−50 to −78	11	1	.245	136–139	.75
13	0.7	0.7	M, .01 W, .003	−50 to −78	11	0.1	.032	135–140	.88
14	0.6	0.6	M, .01 W, .003	−50 to −78	11	0.2	.033	136–140	.5
15	2.0	2.0	A, .05	−55	8	1	.012		
16	2.0	2.0	E, .05	−55	8	1	.240		.88
17	2.0	2.0	M, .05	−78	10	2	.001		
18	2.0	2.0	M, .05	−50	10	2	.43	135–141	.68

[a] Abbreviations: A, acetone; E, ethanol; M, methanol; W, water. [b] Measured in benzene at 25°. [c] Phillips research grade 1,3-butadiene.

molecular weight of the polymer in an attempt to make it soluble, compounds that form canal complexes with urea but do not polymerize extensively when irradiated while complexed were added to the vinyl chloride. The addition of vinyl bromide did not alter the solubility of the polymer. There was no evidence from the infrared spectra for incorporation of vinyl bromide into the polymers; however, a lower discoloration temperature (100°) suggested the possibility of some -CH_2-CHBr- groups.

Incorporation of ethyl chloride into the vinyl chloride-urea complex did alter the solubility of the polymer (Table VI). As the ethyl chloride concentration was increased, yields decreased while the proportion of soluble product increased. The polymer was never completely soluble. Either a nonrandom distribution of ethyl chloride resulted or there was cross-linking. The infrared spectrum of the polymer from the sample with the highest ethyl chloride concentration had a much more intense carbonyl absorption than the other polyvinyl chloride samples. This can be explained by a termination or chain transfer reaction in which the reactive polymer end group attacks the urea in the canal wall. The additional carbonyl absorptions at 5.97, 6.23, 6.42 and 6.9 μ in the infrared spectra of polymers from samples containing ethyl chloride suggest the grafting of urea molecules to the polymer chain. The additional absorptions in the carbonyl region resemble the spectra of N-alkyl ureas (*e.g.*, *n*-butylurea in chloroform absorbs at 6.03, 6.27, 6.41 and 6.86 μ). Further evidence for reaction with urea comes from the 1.6–1.8% nitrogen contents of such samples.

Polymerization of Acrolein.—Acrolein complexed with urea at −78° in the presence of a trace of methanol. The polymer that was isolated after the irradiation of the complex was almost entirely insoluble in polar and non-polar solvents. There was no sharp melting point; the polymer slowly darkened at 200° but did not fuse even at 400°. The infrared spectrum of the polymer contained bands characteristic of ether, hydroxyl, vinyl and carbonyl groups. The product appeared to consist of a variety of units which were similar to those in polymers from acrolein reported previously.[18] The most common units appear to be the 1,4-addition product I, the 1,2-addition product II, the acetal and hemiacetal form of II (III) and crosslinked networks composed of vinyl ether linkages and acetal groups.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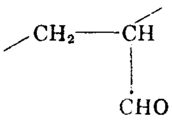
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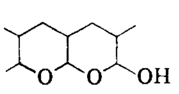
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Copolymerization.—Mixtures of vinyl chloride and acrylonitrile formed complexes with urea. The product that was isolated in low yields after irradiation and extraction of urea was insoluble but did swell in dimethylformamide. The infrared spectrum contained all of the absorption bands of the corresponding homopolymers and no additional bands. The weak absorption at 4.95 μ, corresponding to ketene-imine groups, was more intense than in canal-polymerized polyacrylonitrile.

Other Urea Complexes.—Several potential monomers that were investigated formed complexes

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[18] A. Henglein, W. Schnabel and R. C. Schulz, *Makromol. Chem.*, **31**, 181 (1959); R. C. Schulz, *ibid.*, **17**, 62 (1955–1956); R. C. Schulz and W. Kern, *ibid.*, **18–19**, 4 (1956).

TABLE II

EFFECT OF BUTADIENE CONCENTRATION ON THE POLYMERIZATION OF 1,3-BUTADIENE[a]

Sample	Butadiene, ml.	Polymer wt., g.	Intrinsic viscosity,[b] dl./g.
19	0.33	0.110	1.13
20	.53	.153	1.27
21	.80	0.165, .186	1.45, 1.48
22	1.2	.169, .177	1.33
23	2.0	.174, .175	1.25

[a] For complexes prepared at −55° for 14 days with butadiene (Phillips research grade), 1.00 g. of urea and 0.02 ml. of methanol and then irradiated with a 1.0-Mr. dose. [b] Measured in benzene at 25°.

TABLE III

EFFECT OF DOSE ON THE POLYMERIZATION OF 1,3-BUTADIENE[a]

Sample	Butadiene,[b] g.	Urea, g.	Solvent,[c] ml.	Temp. of complex formation, °C.	Time of complex formation, days	Irradiation dose, Mr.	Polymer, wt., g.	M.p. range, °C.	Intrinsic viscosity, dl./g.
24	0.8	1.0	0.02	−55	12	0.5	0.14		1.8
25	.8	1.0	.02	−55	14	0.5	0.16, 0.17		1.2
26	.8	1.0	.02	−55	5	2.0	.18, .15		1.1
27	.8	1.0	.02	−55	12	2.0	.18		0.9
28	.8	1.0	.02	−55	14	2.0	.20, .20		.9
29	.8	1.0	.02	−55	5	5.0	.20		
30	.8	1.0	.02	−55	12	5.0	.21		.5
31	1.97	1.97	.09	−50 to −78	7	0.1	.1	147–154	1.7
32	2.32	2.32	.09	−50 to −78	7	.5	.23	145–152	
33	1.5	1.5	.06	−50 to −78	14	.5	.29	145 sinters	1.0
34	2.02	2.02	.09	−50 to −78	7	1.0	.27	137–157	
35	2.52	2.52	.09	−50 to −78	7	2.0	.31	132–137	0.8
36	1.5	1.5	.06	−50 to −78	14	5.0	.37	130–131	0.4
37[e]	60	50	.60	−55	12	[d]	8.4	140 sinters	1.2

[a] Additional examples can be found in Tables II and IV. [b] Phillips research grade 1,3-butadiene for runs 24 to 30 and 37; Matheson C.P. butadiene for runs 31 to 36. [c] Methanol was used for samples 24 to 30; 56% aqueous methanol for 31, 32, 34 and 36; 50% aqueous methanol for 33 and 35. [d] The irradiation dose for the large scale preparation was equivalent to a 1.0-Mr. dose for each of fifty-five 2-g. samples. [e] *Anal.* Calcd. for C_4H_6: C, 88.9; H, 11.1. Found: C, 88.6; H, 10.7.

with urea but yielded only traces of polymer after irradiation. Table VII lists these monomers and some which did not complex under the experimental conditions.

Experimental

Preparation of the Canal Complexes.—Reagent grade urea was recrystallized three times from water and ethanol. The monomers and solvents were redistilled and constant boiling center cuts were used. The 1,3-butadiene was Matheson Chemical pure grade (99 mole %) and Phillips research grade (99.8 mole %).

Complexes were prepared by adding the solvent to finely powdered urea, stirring the moistened urea to evenly distribute the solvent, cooling the mixture to −78° and adding precooled (−78°) monomer to the urea–solvent mixture. In the experiments in which known impurities were employed, they were added to the slurry at this point. The samples were stored in a low-temperature bath for periods ranging from several days to several weeks. The complexes, once formed, were dry, fluffy powders. The quantities of reagents, temperature conditions and times of storage are listed in Table I to VII.

Polymerization in the Complexes.—For a small-scale preparation the urea–monomer complex was cooled to −78°, distributed evenly over the surface of a precooled 2-inch (internal diameter) aluminum dish and covered with aluminum foil. The sample was irradiated with an 800-kvp. beam from a 1-mev. General Electric X-ray type resonant transformer. During the transfer of the sample to the aluminum dish and during irradiation, a low temperature was maintained by placing the dish directly over Dry Ice (for the transfer) and over an aluminum block packed in Dry Ice (for the irradiation).

For a larger scale preparation, the urea–monomer complex was cooled to −78° and distributed over an aluminum tray (2 × 50 inches; cooled over Dry Ice), covered with aluminum foil and passed on a motor-driven trolley into the electron beam at a rate calculated to provide doses equal in rate and quantity to the doses given small scale samples.

The same beam intensity was used in all the irradiations, and was such as to give a dose rate of 2.3×10^5 roentgen per second on a 2-g. sample. For the cases in which the sample sizes were larger, the effective dose rates were slightly smaller.

Isolation of the Polymer.—The irradiated complex (at −78°) was transferred to a flask, aqueous acetone (25 to 50% acetone at 25°) was gradually added with swirling and the suspension was left at 25° for at least 2 hours. The polymer was isolated by filtration, the aqueous acetone washing procedure was repeated until urea was no longer present in the washings, and the polymer was dried *in vacuo*. A continuous extraction with acetone in a Soxhlet extractor was used for the acrylonitrile polymers after initially treating the complex with aqueous acetone.

TABLE IV

EFFECT OF *n*-BUTANE ON THE POLYMERIZATION OF 1,3-BUTADIENE[a,b]

Sample	*n*-Butane,[c] ml.	Irradiation dose, Mr.	Polymer wt., g.	Intrinsic visc.,[d] dl./g.
38	1	2	0.159	0.73
39	2	2	.146	.55
40	5	2	.067	.39
41	2	0.5	.056	.84
42	5	0.5	.023	.40

[a] Complexes were prepared at −55° for 14 days with *n*-butane, 0.80 g. of butadiene (Phillips research grade) 1.00 g. of urea and 0.02 ml. of methanol. [b] For comparable examples without butane, see Table III samples 24, 25, 27 and 28. [c] Approximate volume of gas at 740 mm. and 25°. [d] Measured in benzene at 25°.

Characterization of the Polymeric Products.—The yields, melting points, analyses and intrinsic viscosities of the reaction products are presented in Tables I to VII. Various other determinations are listed below.

Hanus solution[9] was used for the titration of the polybutadiene. Since the polymer precipitated when the chloroform solution of polymer was added to the reagent, the reaction time was extended to 17 hours in addition to the normal 0.5 hour. The quantity of IBr consumed was 89% of theoretical after 0.5 hour and 95% after 17 hours. The reaction products were isolated by separating the organic portion of the titration mixture from the aqueous layer, washing the organic portion with water, evaporating the

TABLE V

POLYMERIZATION OF ACRYLONITRILE IN UREA COMPLEXES[a]

Sample	Acrylonitrile, ml. at 25°	Methanol, ml.	Time of complex formation days	Polymer wt., g.	Intrinsic visc.,[b] dl./g.
1	2.0	0	18	0.49	
2	2.0	0.02	18	.51	
3	2.0	.05	8	.63	
	2.0	.05	8	.68	
4	2.0	.2	18	.43	
5	2.0	1.0	5	Trace	
6	0.5	0.05	8	0.21	1.01
7	0.5	.1	8	.20	
8	1.0	.05	8	.32	
	1.0	.05	7	.40	
9	2.0	.05	7	.60	
10	3.0	.05	8	.68	1.5
	3.0	.05	7	.76	
11	4.0	.05	7	.87	
12	5.0	.05	7	1.08	
13	6.0	.05	7	1.05	2.62
14	7.0	.05	7	1.10	
15	8.0	.05	7	1.22	2.86
16	9.0	.05	7	1.19	
17	10.0	.05	7	1.02	2.86
18[c]	3.0	.05	7	0.03	
19[d]	1.25	.02	13	0.32	

[a] All complexes except no. 19 were prepared at −78° from 2.0 g. of urea; the irradiation dose was 2 Mr. [b] Determined in dimethylformamide at 25°. [c] On the third day of complex formation 7.0 g. of chloroprene was added; no chlorine was detected in the polymeric product. [d] Prepared at −55° with 1.25 g. of urea.

TABLE VI

POLYMERIZATION OF VINYL CHLORIDE IN UREA COMPLEXES

Sample	Vinyl chloride, ml.	Urea, g.	Methanol, ml.	Vinyl bromide, g.	Ethyl chloride, g.	Time at −55°, days	Irradiation dose, Mr.	Polymer weight, g.
1	3.0	2.0	0.05			7	5	0.221
2	3.0	2.0	.05			4	2	.158
3	3.0	2.0	0			21[a]		
4	0.82	1.22	0.03			4	2	.216
5	1.03	1.03	.025			4	2	.166
6	1.19	0.88	.02			4	2	.001
7	1.40	0.70	.017			14[a]		
8	0.71	1.22	.03			2.9	2	.132
9	.71	1.22	.03			1.7	2	.113
10	.71	1.22	.03			1.0	2	.063
11	.80	1.13	.03	0.01		5	10	.181
12	.79	1.13	.03	.04		5	10	.107
13	.73	1.13	.03	.14		5	10	.103[b]
14	.81	1.13	.03		0.007	16	5	.034[c]
15[d]	.77	1.13	.03		.048	16	5	.019[c]
16[e]	.54	1.13	.03		.28	16	5	.008[c]

[a] No complex formed. [b] Melting point 100° dec. [c] Partially soluble in polyvinyl chloride solvents (14 < 15 < 16). [d] *Anal.* Found: N, 1.6. [e] *Anal.* Found: N, 1.8.

chloroform and drying at 0.02 mm. The products were white powders which began to decompose on heating at 110° (0.5-hour run) and 105° (17-hour run). The infrared spectra of both products were similar; absorption occurred at 3.44(m), 3.53(w), 5.72(m), 6.93(s), 7.29(w), 7.75(w), 8.10(w), 8.25(s), 8.97(m), 9.80(w), 10.35(w), 13.10(m) μ. The 5.72 μ band is characteristic of an acetate group and indicates appreciable solvolysis possibly during the addition reaction. The 10.35μ band for the 17-hour sample indicated that 5% of the absorption due to the initial disubstituted *trans* double bond remained.

The infrared spectrum of *trans*-1,4-polybutadiene in a KBr pellet had absorption bands at 3.33(w), 3.39(w), 3.45(m), 3.52(m), 6.89(m), 7.48(w), 7.65(w), 8.09(m), 8.92(w), 9.48(m), 10.37(s), 13.96(m) μ. The X-ray powder pattern of *trans*-polybutadiene after acetone extraction of the irradiated complex had 7 bands. The corresponding "d" spaces were 3.95(s), 2.95(w), 2.27(w), 2.21(w), 2.10(vw), 2.01(vw) and 1.76(vw) Å. When a solution of *trans*-polybutadiene was slowly concentrated at room temperature "crystals" of polymer gradually formed. The solvent was filtered from the solid, the solid was dried *in vacuo* and a powder pattern was obtained. The 28 rings corresponded to "d" spacings of 6.02(w), 3.94(vs), 3.62(m), 3.40(vw), 3.20(m), 2.96(s), *2.87*(vw), *2.70*(vw), 2.58(w), *2.50*(w), 2.30(m), *2.24*(w), 2.20(m), 2.14(w), 2.09(w), 1.99(w), *1.94*(w), 1.90(w), 1.77(m), *1.68*(vw), 1.62(vw), 1.52(vw), 1.42(vw), 1.33(vw), 1.29(vw), 1.20(w), 1.17(w) and 1.12 (vw) Å. An identical pattern which lacked the "d" spacings that are italicized above was obtained for *trans*-polybutadiene by evaporating the benzene solution of polymer to dryness.

The infrared spectrum of the polyvinyl chloride in a KBr pellet had absorption bands at 2.95(w), 3.4(shoulder), 3.46(m), 5.77(m), 5.89(w), 6.25(w), 6.55(w), 7.00(s), 7.25(w), 7.42(shoulder), 7.50(m), 7.98(s), 8.16(s), 8.4(w), 8.74(w), 9.08(m), 9.2(shoulder), 10.42(s), 12.05(m), 15.77(m), 16.66(s) μ. The 5.5 to 6.5μ region varied considerably with the method of workup. Extensive extraction with acetone increased the 5.77μ band and decreased the 5.89μ. Polymerization in the presence of ethyl chloride increased the absorption at 3.0, 5.97, 6.23, 6.42 and 6.9μ but decreased absorption at 9.05 and 12.05μ almost entirely. The X-ray powder pattern of the polyvinyl chloride had 6 rings with "d" spacings of 2.2(w), 2.5(w), 2.9(diffuse), 3.5(s), 4.7(m) and 5.2(m) Å.

The infrared spectrum of the polyacrolein in a KBr pellet had absorption bands at 2.92(s), 3.43(s), 3.5(shoulder), 3.68(w), 5.82(s), 6.05(m), 6.5(w), 6.85(s), 7.15(m), 7.35(m), 7.52(m), 8.55(m), 9.7 (s, broad), 10.85 (shoulder), 12.08 (m) μ. When treated with Tollens reagent a black deposit formed on the surface of the polymer. A small portion of the polyacrolein was soluble in hot dimethylformamide and was precipitated by adding the solution to water. The precipitate began to discolor when heated to 200°.

The infrared spectrum of the polyvinyl bromide in a KBr pellet had absorption bands at 3.0(m), 3.46(m), 3.54(w), 6.0(m), 6.53(w), 7.04(m), 7.28(w), 7.42(w), 7.60(m), 8.26(s), 8.7(w), 9.2(w), 10.69(m), 12.13(w) μ.

Acknowledgment.—The author wishes to thank Dr. J. F. Brown, Jr., for many helpful discussions

TABLE VII

MISCELLANEOUS MONOMER–UREA MIXTURES

Monomer	Monomer vol., ml.	Urea, g.	Methanol, ml.	Temp. of complex formation, °C.	Time of complex formation, days	Product[a] weight, g.
Acrolein	2.0	2.0	0.05	−78	8	1.15
Perfluorobutadiene	2.0	2.0	.05	−78	5[b]	
Perfluorobutadiene	2.0	2.0	.05	−55	20[b]	
Ethylene oxide	2.0	2.0	.05	−78	5[b]	
Vinyl acetylene	2.0	2.0	.05	−78	10	0.001[c]
Allyl cyanide	2.0	2.0	.05	−78	10[b]	
Vinyl methyl ether	2.0	2.0	.05	−10	50	0
Vinyl bromide	2.0	5.5	.1	−10	3	0.008
Vinyl bromide	5.0	4.0	.1	−10	35	<.001
Vinyl bromide	5.0	4.0	0	−10	35	<.001
Propylene	3.0	2.0	0.05	−55	7[b]	
Propylene	4.0	2.0	.05	−71	30[b]	
Monoepoxybutadiene	1.0	1.25	.03	−10	8	0
Monoepoxybutadiene	1.0	1.25	.03	−55	8	0
Ethylene	[d]	2.0	[d]	−78	2[b]	
Cyclopropane	1.0	2.0	[e]	−25	2[b]	
Cyclopropane	2.5	2.0	0.04	−55	1	0

[a] The acetone-water insoluble product after irradiation of the complex at −78° with a 2-Mr. dose. [b] A complex did not form. [c] Melting point 135° dec. [d] Ethylene was bubbled through a suspension of urea in 5 ml. of isopropyl alcohol at −78° for 2.5 hours at a rate of 4 ml. per minute. [e] The solvent was 4 ml. of acetone and 3 ml. of water.

and constructive criticisms. Thanks are also due to Mrs. N. R. Young for technical assistance, Mr. J. S. Balwit for the irradiations, Mr. C. A. Hirt and Miss D. V. McClung for the infrared spectra and Mr. H. W. Middleton for the microanalyses.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, QUEEN MARY COLLEGE, UNIVERSITY OF LONDON, LONDON, ENG.]

New Heteroaromatic Compounds. Part VI. Novel Heterocyclic Compounds of Phosphorus

BY M. J. S. DEWAR[1] AND VED P. KUBBA[1]

RECEIVED FEBRUARY 27, 1960

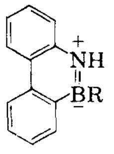
In continuation of previous work we have prepared a number of novel heterocyclic analogs of phenanthrene containing nitrogen and phosphorus in the 9- and 10-positions. The spectra of these compounds resemble those of analogous borazarophenanthrene derivatives, suggesting that they too may be aromatic.

Previous papers[2] of this series have described a number of heteroaromatic boron compounds, each being derived from a normal aromatic by replacement of one carbon atom by the isoelectronic ion B^- and a second by N^+ or O^+, giving a neutral molecule isoconjugate with the normal aromatic.

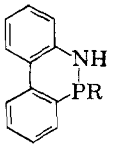
The equality of bond lengths in the phosphonitrile chloride trimer[3] and the general properties of the phosphonitrile chlorides suggest that these compounds are resonance stabilized. The resonance involves *d*-orbitals of the phosphorus atoms, the π-bonds being of $d\pi$–$p\pi$ type. It occurred to us that we might be able to prepare a series of aromatic phosphorus compounds analogous to the boron compounds we had previously prepared by replacing a carbon atom in an aromatic system by the ion P^- in the configuration $(1s)^2(2s)^2(2p)^6(3s)^2(3p)^3(3d)$; aromatic hydrocarbons contain π-MO's built up by the interaction of singly occupied $2p$-AO's of the individual carbon atoms and P^- with a singly occupied $3d$-AO might be a good substitute.

The situation is in fact more complicated than this simple argument implies since phosphorus has a number of *d*-orbitals available for π-bonding, and it seems very likely[4] that in the phosphonitrile chlorides each phosphorus atom uses two different *d*-orbitals to form $d\pi$–$p\pi$ bonds to the adjacent nitrogen atoms. In that case the phosphonitrile chlorides should not be classed as aromatic; for the π-electrons in them occupy isolated three-center π-MO's rather than the cyclic many-center π-MO's characteristic of aromatic systems.

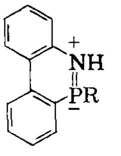
Nevertheless it seemed of interest to prepare heterocyclic compounds of the type indicated above and to study their properties. The phenanthrene system was an obvious choice since we already had a number of analogous borazarophenanthrenes (I) to provide comparison spectra, etc., and since the synthetic difficulties were likely to be less.[2a] We therefore decided to prepare compounds of the type indicated in II; the relation of these to I is indicated by the possibility of writing dipolar resonance structures, *e.g.*, III, in which the double bond to phosphorus is a $d\pi$–$p\pi$ bond.



I



II



III

For reasons indicated above we decided to synthesize derivatives of 9,10-dihydro-9,10-azaphos-

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