Stereospecific Polymerization in Thiourea Canal Complexes[1]

BY JOHN F. BROWN, JR., AND DWAIN M. WHITE

The use of thiourea canal complexes as molecular templates for carrying out selective and stereospecific polymerization reactions was investigated. A polymerization technique was developed which involved forming a canal complex from a mixture of monomer and thiourea, irradiating this to initiate polymerization, and then extracting the thiourea to leave pseudomorphic hexagonal needles of the stereoregular polymer formed. These polymerizations showed various characteristics, for example, sensitivity to inert impurities but insensitivity to dose rate, expected for the polymerization of physically isolated sequences of specifically positioned monomer molecules in canals. High melting, crystalline, trans-1,4 addition polymers were obtained from 2,3-dimethylbutadiene, 2,3-dichlorobutadiene, 1,3-cyclohexadiene and cyclohexadiene monoxide. Isobutylene and vinylidene chloride could also be polymerized in the canals, but gave the expected normal polymers. Cyclopentadiene and cycloöctatetraene were not easily polymerized alone, but could be copolymerized. Numerous other monomers could not be polymerized at all, even in cases where they did form canal complexes. The scope of thiourea canal complex polymerization is thus quite sharply restricted by substrate specificity, a limitation which is probably inherent in any type of template controlled reaction whether biological or synthetic.

This study was undertaken in order to investigate the possibilities of using inclusion compounds as templates for carrying out selective and stereospecific reactions. The reactions studied were the polymerizations of various olefins, dienes and epoxides. It was reasoned that the long, regular holes which exist in canal complexes should be templates for the stereospecific polymerization reactions which would lead to long, regular, unbranched polymer molecules.

We were successful in carrying out polymerizations in the simple canals of urea and thiourea complexes, and also in the branched and intersecting canals of a Linde 5A molecular sieve. The polymers of 1,3-butadiene and vinylacetylene formed by the latter procedure showed no structural regularity, however, and will not be discussed further. The characteristics of polymerizations in thiourea canal complexes will be described in this paper, and those of urea canal complex polymerizations in the following one.[2]

Results and Discussion

Thiourea Canal Complex Formation.—The gross structures of thiourea canal complexes have been described by Schlenk.[3] In these complexes the thiourea molecules are arranged as in the walls of a honeycomb, leaving long hexagonal holes. The unit cell contains six thiourea molecules and a 12.5 Å. length of hole, which is about 6–7 Å. in diameter. Usually, the molecules of the included species fit into the hole end to end; and hence their length determines the stoichiometry of the adduct. These "guest molecules" have fixed position in the canals in that molecular rotation does not occur.[4] It should be noted that the hexagonal crystal structure of the canal complexes is not stable unless the guest molecules are present to fill up the canals; in the absence of adduct former thiourea forms tetragonal crystals having no canals.

The formation of a thiourea canal complex probably requires that the guest molecules be capable of packing snugly into a 6–7 Å. hole. It is still not possible to predict or rationalize this property with any precision. There have been several publications

listing compounds which are capable of forming thiourea adducts[3,5–7] and we screened over 175 compounds for adduct formation during the present study. The only conclusion which seems permissible at this time is that thiourea complex formers can be grouped into five broad classes: 1, Polymethylated, polychlorinated or polybrominated alkanes and their derivatives; 2, derivatives of cyclopentane or its heterocyclic analogs; 3, derivatives of cyclohexane or its heterocyclic analogs; 4, miscellaneous cyclic and bicyclic compounds; 5, small flat molecules (< 3.7 Å. thick).

There are many compounds in all of these categories which do not form complexes, however.

Before this investigation, the existence of the last class of complex formers was not recognized, and it was possible to make the generalization that all molecules which are capable of complex formation have cross-sectional areas of approximately 5.8 × 6.8 Å.[7] The "small flat molecules" are not only considerably thinner than this, but they also differ from the other classes of adduct formers in that the lengths of canal occupied per molecule are considerably shorter than the lengths of the molecules. These deviations in space-filling characteristics from those of a "normal" complex former like cyclohexane are shown in Table I.

TABLE I

DIMENSIONS OF SPACE OCCUPIED BY SOME THIOUREA COMPLEX FORMERS[a]

Compound	Mole ratio of complex	Length of canal occupied	Length of molecule	Cross section, Å.
Cyclohexane	3.0[6]	6.3	6.2	4.8 × 6.9
Cyclopentane	2.4[3]	5.0	5.6	3.8 × 5.8
Cyclopentene	2.2[3]	4.6	5.5	3.6 × 5.8
Dimethylbutadiene	2.75[8]	5.7	7.2	3.6 × 5.8
Isobutylene	...	..	5.6	3.6 × 5.8

[a] Estimated from Courtauld models.

It is probable that in the canal complexes of small flat molecules the guest molecules are not lined up end to end in the canals, but are packed in some sort of overlapping arrangement. It is even possible

(1) Presented before the 133rd Meeting of the American Chemical Society, San Francisco, Calif., April, 1958.

(2) D. M. White, THIS JOURNAL, 82, 5678 (1960).

(3) W. Schlenk, Jr., Ann., 573, 142 (1951).

(4) D. F. R. Gilson and C. A. McDowell, Nature, 183, 1183 (1959).

(5) B. Angla, Compt. rend., 224, 402 (1947).

(6) O. Redlich, C. M. Gable, L. R. Beason and R. W. Millar, THIS JOURNAL, 72, 4161 (1950).

(7) R. W. Schiessler and D. Flitter, ibid., 74, 1720 (1952).

(8) H. Clasen, Z. Elektrochem., 60, 982 (1956).

that the smallest molecules in this category, such as isobutylene and vinylidene chloride, may lie directly on top of each other as in a stack of coins. In either case, this sort of overlapping arrangement would greatly facilitate reaction between the guest molecules. It is noteworthy that almost all of the monomers which were successfully polymerized in thiourea canals were small flat molecules belonging to the above class 5.

Monomers Polymerizable in Thiourea Canal Complexes.—Upon irradiating the canal complexes of various monomers with ionizing radiation, fair to good yields of crystalline polymers were obtained from 2,3-dimethylbutadiene, 2,3-dichlorobutadiene, 1,3-cyclohexadiene and vinylidene chloride. Low yields of polymers were obtained from cyclopentadiene, cyclohexadiene monoxide, 2-chloropropene, 2-bromopropene and isobutylene. The main product obtained from cyclopentadiene was the ordinary endo dimer, again supporting the idea of a high degree of overlapping in the canals. No trace of polymer was obtained from a group of 17 other complexable monomers, which included such species as bicycloheptadiene, cycloheptadiene, cycloöctatetraene, cyclohexene oxide and perfluorobutadiene. In all of these experiments the irradiation was administered as a short burst of high intensity (2.3 × 10⁵ r./sec.) radiation; at this high dose rate virtually no polymerization will occur in any monomer in the liquid phase.

The possibilities of forming copolymers by irradiating the complexes formed from mixtures of monomers were also investigated. It was found that the three possible binary combinations between 2,3-dimethylbutadiene, 2,3-dichlorobutadiene and 1,3-cyclohexadiene all gave copolymers. Cyclopentadiene, which could be homopolymerized only with difficulty, gave good yields of copolymers with dichlorobutadiene and cyclohexadiene, and a poor yield of copolymer with dimethylbutadiene. Cyclooctatetraene, which did not homopolymerize at all, did give copolymers with dichlorobutadiene and cyclohexadiene. Vinylidene chloride was less readily copolymerized. Its mixture with 1,3-cyclohexadiene did give a copolymer, but the mixture with cyclopentadiene gave a nearly pure homopolymer of vinylidene chloride, that with 2,3-dichlorobutadiene gave a nearly pure homopolymer of the diene, and that with 2,3-dimethylbutadiene gave no polymer at all. Attempts to copolymerize 1,3-cyclohexadiene with 6-(2-furyl)-fulvene or N,N'-difurfural-p-phenylenediamine, or 2,3-dichlorobutadiene with isoprene, yielded nearly pure diene homopolymers in all cases.

This copolymerization behavior indicates that the packing of monomer molecules into thiourea canals is not the purely random process which might be expected if no overlapping occurred. Some monomer mixtures do give mixed sequences in the canals, but in other mixtures there is enough segregation so that homopolymers can be formed. Similar behavior was observed in experiments where small amounts of non-polymerizable guest molecules were added to the monomer in order to serve as chain stoppers. It was found that 2% added dimethylbutane was less effective at interrupting

the polymerization of dimethylbutadiene than was 1%, implying that considerable segregation of the saturated hydrocarbon molecules occurred at the higher concentration.

Characteristics of Polymerizations in Thiourea Canals.—It is quite difficult to initiate polymer chain growth inside the crystal lattice of a canal complex by conventional means. For example, when a dimethylbutadiene-thiourea complex was held for two weeks at 120–180° under 2000 atm. pressure only a rubbery polymer, presumably formed outside the canals, was obtained.[9] We were unable to initiate the polymerization of dimethylbutadiene in thiourea canals by heat, ultraviolet light, conventional initiators or combinations thereof. It has been reported, and also observed by us, that some samples of dimethylbutadiene-thiourea complex will polymerize spontaneously on long standing. However, the polymers thus obtained melt about 50° lower than those obtained by deliberate initiation, and hence must have been formed by some process which was at least partially nonstereoselective.

High energy radiation, however, would be expected to penetrate the crystal lattice and generate reactive fragments within the canals. We used such radiation (β- or X-rays) for initiating polymerization throughout this investigation. The initiation efficiency was roughly estimated as $G = 13$ chains formed per 100 ev. during the early stages of polymerization. In a typical dimethylbutadiene polymerization, a 1-Mr. dose gave a 50% conversion to polymer, while a 5-Mr. dose gave a 70% conversion. Evidently, the initiation efficiency dropped off sharply with increasing dose. However, in sharp contrast to the behavior of polymerizations in urea canal complexes,[2] the molecular weights of the polymers obtained from the higher doses were no lower than those obtained from low doses. This may have been related to the fact that the highest molecular weights obtained from thiourea canal complex polymerizations were fairly low anyway (ca. 20,000), and only about one-tenth as high as those obtainable in urea.

The yield and quality of poly-(dimethylbutadiene) obtained from a given dose of irradiation was virtually independent of temperature over the range −78° to +30° and of dose rate over the range 2.9 r./sec. to 2.3 × 10⁵ r./sec. This behavior, indicative of the absence of bimolecular interactions between growing chains, is what would be expected for the polymerization of physically isolated sequences of monomers in the canals. Chain growth in the canals probably occurs very rapidly; when polymerizable thiourea complexes were irradiated a sharp temperature rise due to the heat of polymerization occurred immediately. The sharp temperature rise was observed also for the polymerization of butadiene in a 5 Å. molecular sieve.

The canal complex polymerizations were quite sensitive to impurities in the canals and irregularities in crystal lattice. Freshly prepared dimethylbutadiene-thiourea complexes gave very low yields

(9) British Patent 737,235 (to Metallgesellschaft Aktiengesellschaft), Sept. 21, 1955.
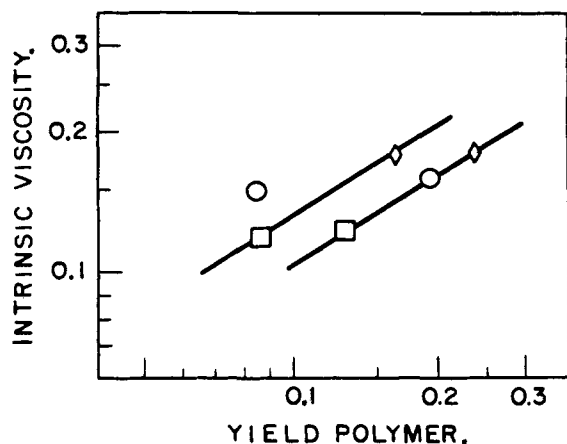
Fig. 1.—Plot of intrinsic viscosity of polydimethylbutadiene as a function of polymer yield from 2.0 g. of complex: upper line, 1 Mr. dose; lower line, 5 Mr. dose; ◊, complexes from 2,3-dimethylbutadiene alone; □, complexes of dimethylbutadiene plus 1% dimethylbutane; O, complexes of dimethylbutadiene plus 2% dimethylbutane.

of polymer upon irradiation, and the normal yields were not obtained unless the complexes were allowed to stand in contact with their mother liquors for two days at 5° before irradiation. The solvent used to assist complex formation also had an appreciable influence on the yield and quality of the polymer obtained.

When a little 2,6-di-t-butyl-p-cresol was added to the monomer to inhibit possible autoxidation during complex formation, a sharp drop in the polymer yield was noted. This prompted a series of experiments in which complexes of dimethylbutadiene containing small quantities of dimethylbutane were polymerized. The results (Fig. 1) showed that the yields and molecular weights of the polymers obtained were both reduced. Further, there was a linear relationship between log [η] and log yield, indicating a direct proportionality between yield and molecular weight. This is what would be expected if the number of chains initiated by the irradiation remained the same, but chain propagation could be blocked by an inert alkane molecule in the sequence of polymerizable diene molecules in the canal. From these inhibition experiments, it is possible to estimate the lengths of the polymerizable sequences in carefully prepared dimethylbutadiene complexes as 100–200 monomer units.

Characteristics of Polymers Prepared in Thiourea Canals.—The poly-(2,3-dimethylbutadiene) obtained by canal complex polymerization was a high melting (267–272°) crystalline polymer, soluble in hot tetralin but readily reprecipitating upon cooling. The infrared spectrum and X-ray diffraction pattern have been shown to be identical to those of the $trans$-1,4-poly-(2,3-dimethylbutadiene), m. 253–259°, obtained by use of a Ziegler catalyst system.[10]

The 2,3-dichlorobutadiene polymer was also a highly crystalline material, soluble only in hot solvents, which could not be melted without decomposition. The infrared spectrum indicated

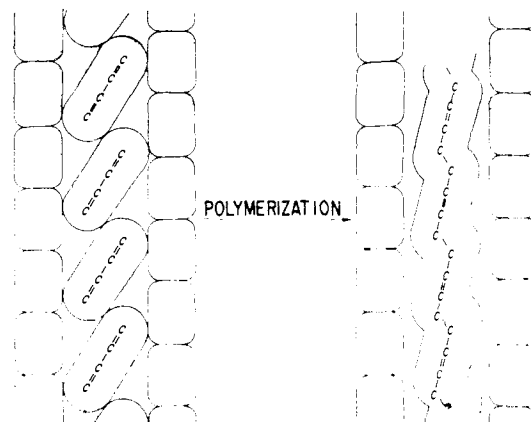(10) T. F. Yen, *J. Polymer Sci.*, **38**, 272 (1959).

Fig. 2.—Schematic representation of a 2,3-dimethylbutadiene polymerization in a thiourea canal, drawn approximately to scale. The diene (C=C—C=C) molecules and the thiourea molecules are viewed edgewise.

the absence of 1,2- or cis-1,4-addition, and the X-ray identity period of 4.86 Å. was that expected for a $trans$-1,4-poly-(2,3-dichlorobutadiene).

The 1,3-cyclohexadiene polymer (m. 370–380°) also appeared to be formed by $trans$-1,4-addition. It differed from the other diene polymers in that it soon lost much of its solubility in hot solvents and X-ray crystallinity upon standing. The polymer of cyclohexadiene monoxide (m. 215–222°) was not investigated in detail, but it appears to be a $trans$-1,4-polyether. The isobutylene and vinylidene chloride polymers formed in thiourea canals did not differ from those prepared by conventional methods; stereoisomerism is not possible in these polymers.

The presumably stereospecific copolymers of monomers having approximately the same size and shape, e.g., the dimethylbutadiene–dichlorobutadiene and the cyclopentadiene–cyclohexadiene copolymers, were high melting materials. Apparently, isomorphous replacement can occur in the crystal lattices of these polymers. The other copolymers obtained showed normal behavior in being much lower melting than the homopolymers of the individual monomers.

In all cases, the crude polymers prepared by irradiating the canal complexes and then extracting the thiourea were obtained as small needles which preserved the external forms of the hexagonal needles of the canal complexes. The X-ray pattern of a needle of poly-(2,3-dichlorobutadiene) obtained in this way resembled a typical fiber pattern. It showed that the polymer chains were lined up parallel to the axis of the needle and partially crystallized into the polymer lattice. Apparently, when the thiourea is extracted from a polymerized complex, the polymer chains collapse together but do not lose the parallel alignment which they had in the complex.

Conclusions.—The foregoing results have shown that suitably packed monomer molecules can be polymerized to stereoregular polymers inside the canals of thiourea canal complexes. In the case of a dimethylbutadiene or dichlorobutadiene polymerization the relative positions of the molecules before and after polymerization can be estimated

from the complexing ratio and the known dimensions of the monomer, canal and polymer repeating unit. These are shown in Fig. 2. This representation also makes it apparent why the overlapping of the guest molecules in the canals, apparently characteristic of the complexes of small flat molecules, is essential for the polymerization of these monomers.

The main limitation to the scope of canal complex polymerization appears to be one which is inherent in any type of template synthesis, whether biological or non-biological; namely, substrate specificity. Using thiourea canals as the template, only a small number of monomers were found to enter the template at all, and even fewer of these could react once they were there. Apparently, a rather delicate matching between the size and shape of the substrate molecules and the size and shape of the canals must be achieved if polymerization is to occur.

Experimental

Screening for Thiourea Complex Formation.—Compounds were tested for thiourea complex formation by adding a small quantity to a saturated solution of thiourea in 50% aqueous acetone. Complex formation was indicated by the appearance of needle-like crystals, either immediately or upon cooling to 0°, which did not disappear after 1-hr. standing. Thiourea was observed to have a metastable needle-like crystal form which sometimes came out of solution upon rapid cooling; however, these needles differed from the needles of the complex in that they soon reverted to the ordinary granular thiourea crystals if left in contact with the solution.

In reporting the results of these tests, the compounds examined will be grouped according to the classifications given above.

1. Polymethylated, polychlorinated, or polybrominated alkanes, and their derivatives and analogs (other than planar molecules) which gave thiourea complexes were

Acetylene tetrabromide	2,5-Dimethyl-3-hexynediol-2,5
t-Amyl bromide	2,3-Dimethyl-2-nitro-3-
t-Butyl hydroperoxide[11]	nitrosobutane
Carbon tetrachloride	2,2-Dinitropropane
Chloroform	Iodotrichloromethane
Di-t-butyl peroxide	2,3,3,4-Tetramethyl-1,4-
1,1-Difluorohexachloropro-	pentadiene
pane	1,1,1-Trifluoropentachloro-
2,3-Dimethyl-2,3-dinitro-	propane
butane	2,4,4-Trimethylpentene-1

Analogous compounds which did not form complexes under our conditions were

Azobisisobutyronitrile	Isoamyl nitrate
1-Bromo-2-methylbutane	Isopropyl formate
N-t-Butylacrylamide	2-Methyl-3-butyn-2-ol
t-Butyl alcohol	Methyl vinyl sulfone
t-Butyl perbenzoate	2-Nitro-2-nitrosopropane[11]
Decamethyltetrasiloxane	2-Nitropropane
3,4-Dichlorobutene	Octamethylcyclotetrasilox-
2,2'-Dihydroxy-di-2-propyl	ane
peroxide	Pentaerythritol
Diisopropyl ether	Pinacol
Dimethyldioxane	Tetramethylammonium
2,5-Dimethyl-2,5-hexanediol	chloride
Ethyl trichloroacetate	Trichloroacetic acid
Hexamethyldisiloxane	Trichloroacetamide
Hexamethylcyclotrisiloxane	Vinyltrimethylsilane

2. Derivatives of cyclopentane or its heterocyclic analogs (other than flat, planar molecules) which gave thiourea complexes were

Cyclopentane	Cyclopentanone	Cyclopentyl iodide

Compounds of this type which did not complex were

Butadiene sulfone	Hexachlorocyclopentadiene
2,5-Diethoxytetrahydro-	Perfluoro-1,2-dichlorocyclo-
furan	pentane

(11) These compounds appeared to undergo chemical reaction with the thiourea solution.

3. Derivatives of cyclohexane or its heterocyclic analogs (other than flat molecules) which gave thiourea complexes were

1,4-Cyclohexadiene	Methylcyclohexane
Cyclohexane	Nitrocyclohexane
Cyclohexanol	Phenylcyclohexane
Cyclohexanone	2-Phenylcyclohexanol
Cyclohexene	1-Phenylcyclohexene
Cyclohexyl chloride	4-Vinylcyclohexene
Hexahydrobenzoic acid	

Compounds of this type which did not form thiourea complexes were

Carvone	Terpin hydrate
2,2'-Dihydroxydicyclohexyl peroxide[11]	α-Terpineol
Dipentene	Terpinolene
3-Phenylcyclohexadiene-1,4	s-Trioxane

4. Other cyclic and bicyclic hydrocarbon derivatives which formed complexes were

Bicycloheptadiene	Cyclohexadiene oxide
Borneol	Cyclohexene oxide
Camphene	Cyclooctatetraene
Camphor	Dicyclopentadiene
Cineole	1,4-Endoxocyclohexane
Cycloheptatriene	

Compounds of this type which did not form complexes were

Glycidyl methacrylate[11]	Santonin
Methyl cyclopropyl ketone	Tetralin
α-Pinene	

5. Flat molecules (<3.7 Å. thick) which gave complexes were

2-Bromopropene	2,5-Dimethyl-1,5-hexadiene
2-Chloropropene	Hexafluorobutadiene[12]
1,3-Cyclohexadiene	Isobutylene
Cyclopentadiene	Tetrachloroethylene
Cyclopentene	Tetramethylethylene
2,3-Dichloro-1,3-butadiene	Thiophene
N,N'-Difurfural-p-phenyl-	Trimethylene disulfide
enediamine	Vinylidene chloride
2,3-Dimethyl-1,3-butadiene	

Flat molecules which did not give complexes were

Acetylacetone	Hexachlorobutadiene
Acetyl peroxide[11]	Hexafluoro-2,3-dichloro-2-
2-Acetylthiophene	butene
Acrylonitrile	Indene
Allyl chloride	Isoprene
Benzoyl peroxide[11]	Isopropenyl acetate
Biacetyl	Isopropenylacetylene
Butadiene	2,4-Lutidine
1-Butene	2,6-Lutidine
2-Buten-1,4-diol	Maleic acid or anhydride
Butyraldoxime	Mesityl oxide
Chloroprene	Methacrolein
Cyclopropane	Methacrylamide
1,3-Dibromopropane	Methacrylonitrile
cis-1,2-Dichloroethylene	4-Methoxystyrene
trans-1,2-Dichloroethylene	Methacrylic acid
1,3-Dichloropropane	Methallyl methacrylate
1,3-Dichloropropene	Methyl isopropenyl ketone
Diethyl fumarate	Methyl methacrylate
Dimethallyl ether	p-Methyl-α-methylstyrene
2,5-Dimethyl-2,4-hexadiene	2-Methylthiophene
2,5-Dimethyl-1,5-hexadien-	3-Methylthiophene
3-yne	Methyl vinyl ketone
2,5-Dimethyl-1,3,5-hexa-	α-Nitroisobutylene
triene	p-Nitrosodimethylaniline[11]
2,3-Diphenyl-1,3-butadiene	1,3,7-Octatrien-5-yne
1,3-Dithiane	Propargyl alcohol
Divinylacetylene	Propylene
p-Divinylbenzene	Pyridine
Ethyl acrylate	Pyrrolidine
Ethylene oxide[11]	Triallylcyanurate
Formamide	Trichloroethylene
Furan	Vinyl acetate
Furfural	Vinyl bromide
6-(2-Furyl)-fulvene	Vinyl chloride
Fumaric acid	Vinyl ethyl ether
Fumaronitrile	1-Vinylnaphthalene

(12) Below −10° only.

TABLE II

COPOLYMERIZATIONS IN THIOUREA CANAL COMPLEXES[a]

Monomer I[b]	Monomer II[b]	Polymer yield, g.	M.p., °C.	$[\eta]$, dl./g.	Bands of I	Bands of II	Shifted bands	Conclusion
DMB	DCB	0.37	255–320	0.17	+	+	+	Copolymer
DMB	CHD	.12	120–270	0.06	+	+	+	Copolymer
DMB	CPD	.02	140–180		+	+	°	Copolymer
DMB	VDC	.00	.....		–	–	–	No polymn.
DCB	CHD	.25	130–180	0.14	+	+	+	Copolymer
DCB	CPD	.46[d]	160–190	.13	+	+	+	Copolymer
DCB	ISP	.31	220–>280	.15	+	Trace	–	Mainly I polymer
DCB	COT	.05	130–180		+	+	+	Copolymer
DCB	VDC	.25	180–>300	0.15	+	Trace	–	Mainly I polymer
CHD	CPD	.20	320–380	Ins.	+	+	+	Copolymer
CHD	COT	.10	200–290	Ins.	+	+	+	Copolymer
CHD	FUF	.25	.....		+	Trace	–	Mainly I polymer
CHD	DPF	.21	>300		+	Trace	–	Mainly I polymer
CHD	VDC	.35	120–145	0.15	+	+	°	Copolymer
CPD	VDC	.17	d. 160	0.10	Trace	+	–	Mainly II polymer

[a] Prepared from 0.70 ml. of each monomer, 5 ml. of aqueous acetone, 4 g. of thiourea, held 2–3 days at 5°, then complex separated, dried, and 2.0-g. portion irradiated with 5 Mr. at 2.3×10^5 r./sec. [b] Key: DMB, 2,3-dimethyl-1,3-butadiene; DCB, 2,3-dichloro-1,3-butadiene; CHD, 1,3-cyclohexadiene; CPD, cyclopentadiene; VDC, vinylidene chloride; ISP, isoprene; COT, cyclooctatetraene; FUF, 6-(2-furyl)-fulvene; DPF, N,N'-difurfural-p-phenylenediamine, of which only 0.2 g. was used. [c] Spectrum too weak to show bands in 10–15 μ region clearly. [d] This corresponds to a 90% conversion to polymer, since the yield of complex was 5.38 g.

Screening for Polymerization in Thiourea Canal Complexes.—In testing thiourea complexed monomers for polymerizability, the usual procedure was to prepare a slurry of 4 g. of finely ground thiourea (reagent grade, recrystallized from methanol), about 1.5 ml. of monomer or monomer mixture, and 5 ml. of aqueous acetone, and to leave this in a refrigerator at least 2 days to allow the formation of the complex to go to completion. The slurry was centrifuged while still cold to remove the solution, and the remaining moist solid dried over calcium chloride in a small container. The drying step did not appear essential to the success of the subsequent polymerization, and it was omitted with the isobutylene complex in order to minimize loss of the monomer. Next, 2.0-g. portions of the resulting complexes were rapidly weighed out, spread out uniformly in a 20 cm.² aluminum dish, and irradiated with an 800 kvp. electron beam from a G.E. resonance transformer unit at a dose rate of 2.3×10^5 r./sec. for 22 seconds, thus accumulating a dose of 5 Mr. The sample geometry was known from previous work to permit a fairly uniform irradiation dose in the apparatus used. In a few cases the irradiation produced distinctive colorations in the complexes. Finally, the complex was dissolved in water and the polymer, if any, filtered off and washed with water, alcohol, and acetone. In cases where good yields of polymer were obtained, it was sometimes necessary to digest the polymers with acetone for 1–2 hr. in order to complete the removal of thiourea.

Following this procedure, fair to good yields of solid polymers were obtained from 2,3-dimethylbutadiene, 2,3-dichlorobutadiene, 1,3-cyclohexadiene and vinylidene chloride. Low yields of polymers were obtained from cyclopentadiene, isobutylene, 2-bromopropene, 2-chloropropene and cyclohexadiene monoxide. The main product obtained from the irradiated thiourea–cyclopentadiene complex was the ordinary dimer, *endo*-dicyclopentadiene. The thiourea–2-bromopropene and thiourea–2-chloropropene complexes turned blue upon irradiation; when dissolved in water the blue colors disappeared and a little unidentified gas was evolved.

No trace of polymer was obtained from bicyclo[2.2.1]-heptadiene, camphene, cycloheptatriene, 1,4-cyclohexadiene, cyclohexene, cyclohexene oxide, cyclooctatetraene, cyclopentene, N,N'-difurfural-p-phenylenediamine, 1,4-end-oxocyclohexane, hexafluorobutadiene, tetrachloroethylene, tetramethylethylene, 2,3,3,4-tetramethyl-1,4-pentadiene, thiophene, 2,4,4-trimethyl-1-pentene or 4-vinylcyclohexene. The irradiation of the thiourea–cyclooctatetraene complex turned it from yellow to green; upon solution in water the green color disappeared. No trace of water-insoluble material less volatile than cyclooctatetraene was formed.

Copolymerization in Thiourea Canal Complexes.—Mixtures of monomers were tested for copolymerization using the same general method as above. The results are shown in Table II. Copolymerization was concluded to have occurred in cases where the infrared spectrum showed that units derived from both monomers were present in the polymer, and also that (a) there were bands in the 10–15μ region of the spectrum which had shifted from the positions observed in the homopolymers, or (b) marked alteration of the melting point had occurred, or (c) units derived from monomers which did not homopolymerize were present.

Study of Polymerization Variables.—In searching for means of initiating polymerization other than with ionizing radiation, several compounds which might enter into the canals of the thiourea complexes and which might give free radicals upon exposure to heat or light were tested as initiators. These were biacetyl, methyl isopropenyl ketone, di-*t*-butyl peroxide, iodotrichloromethane and trimethylene disulfide. The first two of these do not normally form thiourea complexes by themselves; however, the last three are all good complex formers. In testing them, a 1% solution of the compound in 2,3-dimethylbutadiene was converted to its thiourea complex in the usual way. Portions of these complexes were then subjected to the following treatments: (a) 0.5 hr. directly under an ultraviolet lamp at about 50°; (b) 1 hr. heating in a sealed tube at 100°; (c) 24 hr. standing at 25°; (d) 7 days standing at 25°. Treatments a and d gave traces of polymer from all samples, including those containing no initiators. Treatments b and c gave no traces of polymer in any case.

Using the general experimental procedure employed in the screening study, the effects of varying the monomers, solvents and other addends, crystallization time, irradiation dose and dose rate in various homopolymerizations were studied as shown in Table III. In this table the run numbers group together polymerizations done with the same batches of monomer and thiourea on the same days and under as comparable conditions as possible. The run numbers also show the sequence of experiments done with each monomer, although not the sequence of experiments involving different monomers.

The 2,3-dimethylbutadiene used was prepared by the I$_2$-catalyzed dehydration of pinacol followed by fractionation in a 50-plate Piros–Glover column. This material showed no contaminants detectable by v.p.c.; however, late in the investigation (runs 13, 14) it was discovered that the quality of the polymer could be improved if the monomer were recrystallized at −78° before use. The other monomers used were commercial materials; all monomers were redistilled immediately before use.

Since one early run (4) with no solvent had given a good yield of polymer, an attempt was made to scale up on this basis. In run 12, a mixture of 29.4 g. of 2,3-dimethylbutadiene and 120 g. of finely powdered thiourea was

Table III
Homopolymerizations in Thiourea Canal Complexes[a]

Run	Mono-mer [b]	Ml. per 4.0 g. thiourea	Sol-vent [b]	Ml. per 4.0 g. thiourea	Addend	Time for crystn., days	Dose rate (10⁵ r./sec.)	Dose, Mr.	Yield from 2 g. complex	Polymer m.p., °C.	$[\eta]$, dl./g.
1	DMB	1.1	W–pyr.	5	...	0.02	2.3	3	0.075	232–238	
2	DMB	1.7	W–ac.	5	...	2	0.23	5	.255	243–251	0.17
3	DMB	1.7	W–ac.	5	...	1	2.3	5	.175	240–244	.18
3	DMB	1.7	W–ac.	5	...	1	0.23	5	.175	240–252	.20
4	DMB	2.0	None	..	...	4	2.3[c]	5	.273	252–256	
4	DMB	2.0	None	..	...	5	0.23	5	.282	246–253	
5	DMB	2.0	Ac.	0.5	...	4	2.3[c]	5	.265	250–254	
5	DMB	2.0	Ac.	0.5	...	5	0.23	5	.279	247–253	
6	DMB	2.0	Meth.	0.5	...	4	2.3[c]	5	.281	249–255	
6	DMB	2.0	Meth.	0.5	...	5	0.23	5	.200	247–252	
7	DMB	1.3	W–ac.	4.7	...	1	.23	1	.103	249–252	
7	DMB	1.3	W–ac.	4.7	...	1	.23	3	.142	245–250	
7	DMB	1.3	W–ac.	4.7	...	1	.23	6	.204	244–249	
7	DMB	1.3	W–ac.	4.7	...	1	.23	10	.188	238–244	
8	DMB	1.7	None	..	3%C	1	.23	5	.011	>360 dec.	
9	DMB	1.3	W–ac.	4.7	...	4	2.3	1	.165	229–240	0.18
9	DMB	1.3	W–ac.	4.7	...	4	2.3	5	.207	232–240	.18
9	DMB	1.3	W–ac.	4.7	1%D	4	2.3	1	.087	229–235	.125
9	DMB	1.3	W–ac.	4.7	1%D	4	2.3	5	.131	230–235	.13
9	DMB	1.3	W–ac.	4.7	2%D	4	2.3	1	.085	225–235	.15
9	DMB	1.3	W–ac.	4.7	2%D	4	2.3	5	.195	232–239	.17
10[a]	DMB	1.5	None	..	...	5[a]	1–3	2–4[a]	.173	252–259	.14
13	DMB[f]	1.9	Ac.	0.7	...	7	2.3[d]	2	.25	260–262	.31
13	DMB[f]	1.9	Ac.	.7	...	7	2.3[e]	5	.25	257–261	.31
14[a]	DMB[f]	2.6	W.	.6	...	4	2.3	0.89[a]	.27	266–270	
14[a]	DMB[f]	2.6	W.	.6	...	4	0.000029	1.01[a]	.45	267–272	
15	DCB	1.1	W–pyr.	5	...	1	.46	10	.203	120–180	
16	DCB	0.95	W–ac.	5	...	1	.23	5	.562	240–>285	
16	DCB	0.95	None	..	...	1	.23	5	.560	....	0.21
17	DCB	1.5	None	..	3%C	1	.23	5	.381	>360 dec.	0.16
18[g]	DCB[f]	4.8[g]	Meth.	28[g]	...	5	2.3	1	.563	240–>300	[g]
19	CHD	1.3	W–ac.	4.7	...	1	0.23	5	.425	350–380	
20	CHD	1.0	W–ac.	5	...	1	2.3	5	.251	370–380	
21	CHD	1.8	W–ac.	5	...	2	2.3	1	.176	329–363	
21	CHD	1.8	W–ac.	5	...	2	2.3	5	.335	330–365	
22	VDC	1.2	W–ac.	5	...	12	2.3	5	.009[h]	290 dec.	
23	VDC	2.0	None	..	...	7	2.3	5	None	....	
23	VDC	2.0	Ac.	0.4	...	7	2.3	5	0.263	d. 150–190	
23	VDC	2.0	W.	0.4	...	7	2.3	5	.260	d. 150–190	
23	VDC	2.0	Meth.	0.4	...	7	2.3	5	.141	d. 150–190	
24	VDC	2.0	None	..	...	4	2.3	1	None	....	
24	VDC	2.0	Ac.	0.4	...	4	2.3	1	0.141	d. 120–200	
24	VDC	2.0	W.	0.4	...	4	2.3	1	.138	d. 120–200	
24	VDC	2.0	Meth.	0.5	...	4	2.3	1	.072	d. 120–200	
25	BP	2.0	W–ac.	5	...	5	2.3	5	Trace	....	
26	BP	2.0	W.	0.4	...	6	2.3	5	Trace	....	
26	BP	2.0	Ac.	0.4	...	6	2.3	5	0.009	Liquid	
26	BP	2.0	Meth.	0.4	...	6	2.3	5	.004	....	
27	CP	2.0	W–ac.	5	...	5	2.3	5	Trace	Liquid	
28	CP	2.0	W.	0.4	...	6	2.3	5	Trace	....	
28	CP	2.0	Ac.	.4	...	6	2.3	5	Trace	....	
28	CP	2.0	Meth.	.4	...	6	2.3	5	Trace	....	
29	IB	2.0	Ac.	.5	...	3	2.3[d]	5	0.016	Gum	
29	IB	2.0	Meth.	.5	...	3	2.3[d]	5	Trace	....	
30	CDO	1.1[i]	W–ac.	16	...	1	2.3	2	0.030	215–222 dec.	

[a] Conditions and additional description given in text. [b] Key: DMB, 2,3-dimethyl-1,3-butadiene; DCB, 2,3-dichloro-1,3-butadiene; CHD, 1,3-cyclohexadiene; VDC, vinylidene chloride; BP, 2-bromopropene; CP, 2-chloropropene; IB, isobutylene; CDO, cyclohexadiene monoxide; w., water; pyr., pyridine; ac., acetone; meth., methanol; C, 2,6-di-*t*-butyl-*p*-cresol; D, 2,3-dimethylbutane. [c] Irradiation dish not water cooled. [d] Irradiated at 0°. [e] Irradiated at −78°. [f] Monomer recrystallized at −78° before use. [g] Large crystals of complex prepared in 0.80 g. yield by slowly cooling solution of 1.0 ml. of DCB and 1.0 g. of thiourea in 7 ml. of methanol at 50°. Irradiation gave 0.255 g. of large needles of polymer. These were soluble in boiling tetralin and chlorotoluene, but didn't stay in solution at 160° long enough to permit viscosity measurements. [h] Polymer consisted of a few medium sized needles; most crystals of complex didn't polymerize. [i] 1.07 g. of monomer used; entire yield of complex was irradiated.

prepared and left in the refrigerator. Unexpectedly, there was no indication of complex formation for 5 days, after which it occurred within a few hours to convert the pasty mixture to a fine, white powder of the complex. The complex was placed in a long trough and rolled slowly under the electron beam so as to accumulate a dose which varied between 2–4 Mr., depending upon position in the layer of complex. The results (44% yield of polymer, $[\eta]$ 0.14) were disappointing and prompted a study of the effects of various solvents in facilitating the formation of the crystal-line complex from mixtures of monomers and thiourea. The data obtained with dimethylbutadiene are shown in Table IV; those obtained using vinylidene monomers are shown in runs 23, 24, 26, 28 and 29 of Table III. These data show that a thiourea solvent is necessary if the forma-tion of a polymerizable complex is to occur reliably, and that the nature of the solvent used does have some effect upon the yield, m.p. and intrinsic viscosity of the polymer. Also notable is the fact that the polymers of 2,3-dimethylbutadi-ene obtained in runs 11–14, in which crude moist complex was irradiated directly without prior drying, were higher melting than the polymers prepared in the usual way.

TABLE IV

EFFECT OF SOLVENT ON THE POLYMERIZATION OF 2,3-DIMETHYLBUTADIENE IN THIOUREA[a]

Run	Solvent	Polymer yield, %[b]	Polymer m.p., °C.	$[\eta]$, dl./g.
11	n-Pentane	0	.....	..
11	Dimethylformamide	48	257–265	0.18
11	50–50 water–pyridine	42	256–>300	Ins.
11	Methanol	52	260–263	0.19
11	Ethanol	40	.....	.19
11	Water	47	256–260	.20
11	50–50 water–acetone	50	259–264	.17
11	Acetone	50	262–270	.22
12	Acetone	40	260–265	.20
12	Methyl ethyl ketone	38	250–267	.20
12	Isopropyl alcohol	29	230–260	.20
12	Acetic acid	39	255–261	.17
12	Acetonitrile	47	255–260	.20
12	Pyridine	39	255–268	.22

[a] Mixture of 1.5 g. of thiourea, 0.5 g. (0.7 ml.) dimethyl-butadiene and 0.2 ml. of solvent allowed to stand 5 days at 5°, then irradiated at 2.3 × 10⁵ r./sec. to 1 Mr. without further separation or drying. [b] For comparison with Table III, a 50% yield corresponds to 0.250 g. of polymer. In these runs, where dose was 1 Mr., it also corresponds to a radiation yield $G = 1750$ monomer molecules polymerized per 100 ev.

Since runs 3–6 had shown only a small and uncertain variation in yield resulting from a 10-fold variation in dose rate, a pair of experiments involving a 10⁵-fold variation was carried out as run 14. A mixture of 1.88 g. of finely pow-dered thiourea, 0.28 ml. of water and 1.20 ml. (0.875 g.) of dimethylbutadiene was placed in a glass ampoule, de-gassed by repeated freezing and pumping at liquid nitrogen temperature, sealed off, allowed to stand in the refrigerator 4 days, and then irradiated for 97.4 hours with 50 kv. X-rays at room temperature. The dose rate, estimated by irradiat-ing the same weight of aerated ferrous sulfate solution in the same ampoule, was 10,400 r. per hour; hence, the accumu-lated dose was 1.01 Mr. Extraction of the complex until the infrared spectrum no longer showed thiourea bands gave 0.61 g. (69% yield, $G = 2400$ molecules polymerized per 100 ev.) of polymer, m. 267–272°. A second mixture of the same components was placed in a stoppered test-tube, cooled to liquid nitrogen temperature for a few minutes, and then left in the refrigerator with the first mixture for 4 days. The entire mixture was then transferred to the usual aluminum dish and irradiated with the full 800 kvp. elec-tron beam for the 4.35 sec. usual for a 1 Mr. dose. The actual dose was 0.89 Mr. because of the 50% greater sample size. Extraction of the thiourea left 0.364 g. (42% yield) of polymer m. 266–270°. The comparable experiment in run 11 gave 47% yield of polymer after a 1.0-Mr. dose.

The higher yield of polymer from the slow irradiation experiment may have been due in part to a greater initiation efficiency by X-rays, or to the use of a sealed, deoxygenated system, rather than solely to a dose rate effect.

Lengths of Polymerizable Sequences.—From the data on the yields of polymer obtained from 2,3-dimethylbutadi-ene containing known amounts of 2,3-dimethylbutane, it is possible to estimate minimal values for the lengths N of the polymerizable sequences of monomers in the canals. Let us consider that the canals contain a mole fraction c of randomly distributed canal blocking material (i.e., impurity molecules, crystal dislocations or reactive thiourea molecules;) then, $N_o = 1/c$. If a quantity a of added impurity be also randomly dispersed in the canals then the lengths of the polymerizable sequences will be decreased to $N_a = 1/(c + a)$. For a given small dose of irradiation, the yield X will be proportional to N. Hence $X_o/X_a = (c + a)/a$ and $N_o = (X_o - X_a)/aX_a$.

Applying this treatment to the results of run 9 leads to the following estimates of N_o

Mole fraction dimethylbutane added (a)	Dose, Mr.	X_a	X_o	N_o
0.01	1	0.087	0.165	89
.01	5	.131	.207	85
.02	1	.085	.165	48
.02	5	.195	.207	12

The main limitation on this calculation of N_o is that it requires that the impurity be randomly distributed in the canals. This is obviously not the case for the run 9 experi-ments with 2% dimethylbutane, nor was it the case in the runs where mixtures failed to give copolymers. Hence, even the highest values of N_o can only be taken as minimal values.

The relationship between N_o and the degree of polymeriza-tion $\bar{P}_n$ will be somewhat affected by whether the poly-merizable sequences, once initiated, grow in one or both directions, and also by any radical coupling which may occur when the thiourea is dissolved out. If, however, we assume that the highest minimal value of N_o calculated above is approximately equal to $\bar{P}_n$ for the uninhibited polymeriza-tions, and that the slope (0.65) of the lines in Fig. 1 repre-sents the α in the relation $[\eta] = KM^\alpha$, then we may estimate K as 5.6×10^{-4}, and the molecular weights of typical polydimethylbutadiene samples as

$[\eta]$	0.14	0.18	0.22	0.32
M_n	4600	7000	9600	17200

This estimate implies that $G = 13$ chains formed per 100 ev., which would seem a not implausible value for chain initiation in a thiourea–diene complex.

Characterization of Polymers.—All melting points were taken in evacuated capillaries and reported in Tables II, III and IV. Intrinsic viscosities were all taken in tetralin solution at 150°; many of the solutions were supercooled at that temperature and measurements on the higher melting polymers had to be made promptly.

In all cases where a polymerization in a canal complex gave a solid polymer, the crude product left after extraction of the thiourea was found upon microscopic examination to consist of small needles with well defined crystal faces. These needles were undoubtedly pseudomorphs; however, they did show optical anisotropy, and the smaller ones, at least, showed well defined extinctions when rotated between crossed polaroids, indicating the existence of either strains or molecular orientation with respect to the crystal axis. The X-ray diffraction patterns showed that the polymers obtained were highly crystalline.

The infrared spectra of all the diene polymers and co-polymers revealed the presence of small quantities of hy-droxyl and carbonyl groups. Since these seemed par-ticularly prominent in the polymers obtained in the lowest yield, it is believed that they are associated with end groups. This would imply that the eventual fate of the radical left at the end of a polymer chain was combination with atmos-pheric oxygen. Most of the polymers were occasionally obtained in an insoluble, infusible cross-linked form, and the polymers of 1,3-cyclohexadiene all appeared to become par-tially cross-linked on standing.

2,3-Dimethylbutadiene Polymers.—The colorless to pale tan needles of this polymer melted reversibly over a few

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, 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.

(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.

Stereospecific Polymerization in Urea Canal Complexes[1]

BY DWAIN M. WHITE

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