Cyclopolymerization of 1-Vinyluracil[1]

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ABSTRACT: The free-radical polymerization of 1-vinyluracil has been shown to form substituted dihydrouracil rings in the polymer *via* a cyclopolymerization mechanism. Evidence for this was obtained from the decreased ultraviolet absorption at 265 mμ, the low percentage of uracil 5 and 6 protons in the nmr spectrum, the appearance of a strong dihydrouracil N-3 proton, and the decrease in the number of carbon double bonds by ir. Attempts to trap the cycloadduct by the free radical additions of thiophenol and chloroform to 1-vinyluracil led to normal addition to the 1-vinyl group without cyclization. Structure XIII is proposed for the cyclopolymer based on this information, molecular model studies, and the absence of aziridine protons in the infrared spectrum of poly(3-methyl-1-vinyluracil).

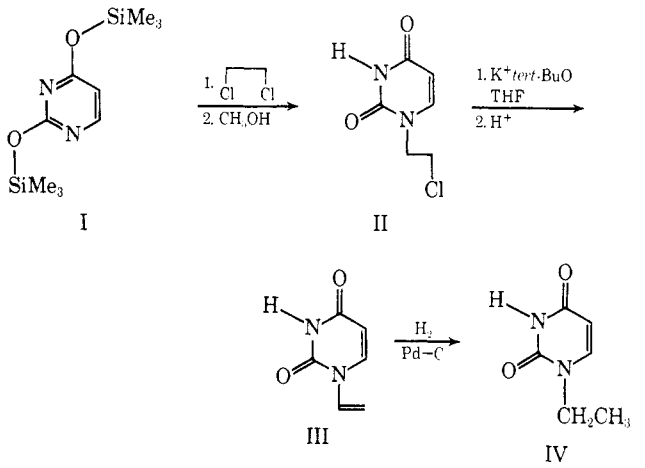
The cyclopolymerization[2] of nonrigid 1,4 dienes such as divinylaniline,[3] divinyl ether,[4] divinyl ketones,[5] 1,4-pentadiene[6] and the copolymerization of some of these monomers with maleic anhydride[7] have been reported to form either bicyclic structures or rings with greater than four members. Rigid bicyclic dienes, on the other hand, such as 5-carboethoxynorbornadiene,[8] have been shown to cyclopolymerize with formation of three-membered rings.

During an investigation of the synthesis and properties of simple vinyl polymers which are analogs of the nucleic acids, we had reason to prepare and polymerize 1-vinyluracil.[9,10] The free radical initiated polymerization of this monomer did not proceed completely in the way we had hoped it would. It is our purpose here to report on the cyclopolymerization of a 1,4 diene which has one of its double bonds rigidly held in a ring and to consider possible structures for the cyclopolymer.

Results and Discussion

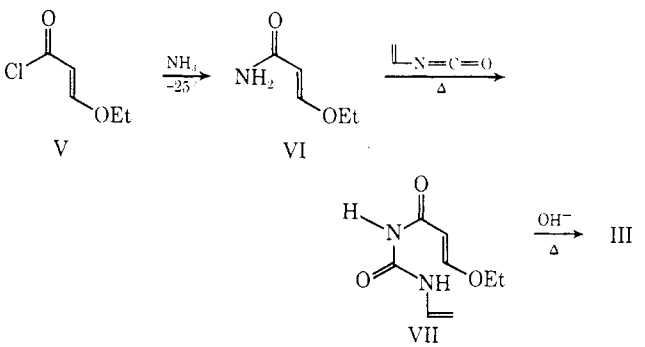
Monomer Synthesis. In our early work,[9] 1-vinyluracil (III) was prepared by two approaches. In the first procedure, a modified Hilbert–Johnson reaction[11] was used to synthesize 1-(2-chloroethyl)uracil (II).[12] 2,4-Bis(trimethylsilyl)uracil[13] was heated in a sealed tube with 1,2-dichloroethane. After hydrolysis of the unreacted trimethylsilyl groups a 9% yield of II was obtained.

Dehydrohalogenation of II was best achieved at 25° in tetrahydrofuran with an excess of potassium *tert*-butoxide.



Unequivocal proof of structure was obtained by the selective hydrogenation[14] of III to 1-ethyluracil (IV).[15] Two other groups have also prepared III by dehydrohalogenation of II.[16,17]

In a second approach to III, β-ethoxyacryloyl[18] chloride(V) was converted into β-ethoxyacrylamide (VI) in 68% yield after treatment with ammonia at −25°. Using the general urea synthesis of Murdock and Angier[19] VI was converted into *N*-β-ethoxyacryoyl-*N'*-vinylurea (VII) in 74% yield by heating with vinyl isocyanate[20] in a sealed tube. Cyclization of VII with aqueous, ethanolic sodium hydroxide followed by chromatography on silicic acid afforded III in 20% yield.



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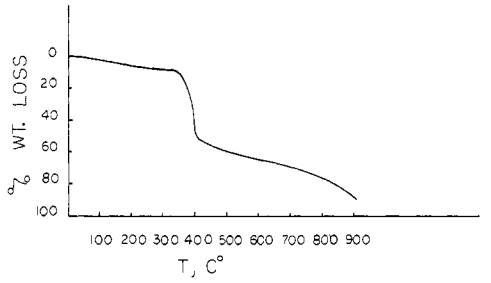

Figure 1. Thermogravimetric analysis of poly(1-vinyluracil) under N_2.

All the methods mentioned above for synthesizing III have now been superseded by our new direct vinylation procedure. The details of this method are reported elsewhere.[10]

Polymerization and Characterization. 1-Vinyluracil was polymerized with potassium persulfate[21] in water at 95° under nitrogen giving a 72% yield of polymer. The poly(1-vinyluracil) (PVU) was shown to be amorphous by X-ray diffraction. Differential thermal analysis of this material did not indicate any first- or second-order transitions up to the decomposition temperature. Thermogravimetric analysis (Figure 1) under nitrogen indicated thermal stability to ≈400°. The gradual loss in weight during the early heating phase is probably due to desorption of water from the hygroscopic polymer.

This polymer was soluble in dimethyl sulfoxide, dilute sodium hydroxide, concentrated hydrochloric acid, and concentrated sulfuric acid, but was only very slightly soluble in water and common organic solvents. Dimethyl sulfoxide was particularly convenient for determining the intrinsic viscosity, $[\eta]$ = 0.14 dl./g, and for casting transparent films which were found to be brittle.

Evidence for Cyclopolymerization. Ultraviolet analysis of the polymer was initially impeded by its low solubility in aqueous buffers. This problem was solved, however, by dissolving the polymer in dilute base, diluting with a large volume of buffer, and then back-titrating to pH 7.0 with dilute acid. A similar method has recently been reported for preparing concentrations as high as 5 mg/ml.[22]

The ultraviolet spectrum of the polymer showed an absorption maximum at 265 mμ as expected; however, the extinction coefficient was only 11% of the reported value for a

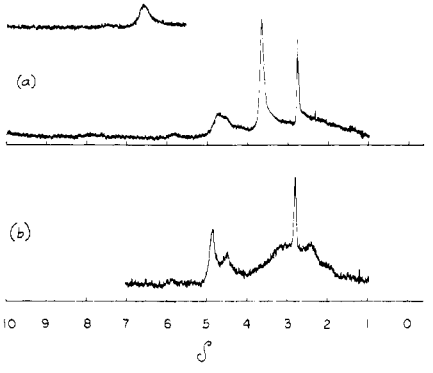

Figure 2. Nuclear magnetic resonance spectrum of poly(1-vinyluracil) in DMSO-d_6: (a) 25°, offset 400 Hz; (b) 148°.

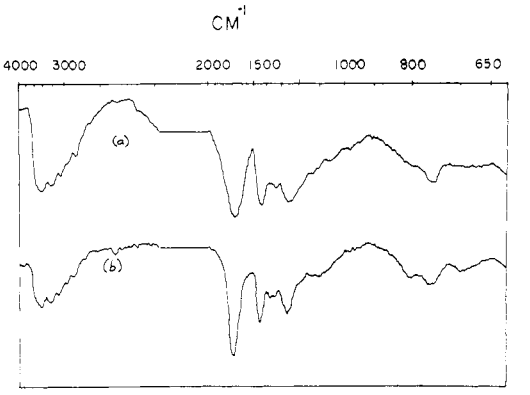

Figure 3. Infrared spectrum of poly(1-vinyluracil) in KBr: (a) prepared at 95°, (b) prepared at 61°.

uracil derivative[23] indicating that addition to the uracil rings had taken place.

Evidence for the formation of 5-substituted dihydrouracil rings was obtained by comparing the ultraviolet spectrum of the polymer with that of 1-ethyl-5-methyldihydrouracil in dilute base. Both materials exhibited an absorption maximum at 240 and 238 mμ, respectively, which decreased in intensity with time because of base-catalyzed ring opening.[24] Uracil rings are not susceptible to ring opening under these conditions.

The nuclear magnetic resonance spectrum (Figure 2a) of the polymer in dimethyl-d_6 sulfoxide was also consistent with substituted dihydrouracil formation as can be seen by the almost complete disappearance of the peaks for the 5- and 6-uracil protons at δ 5.96 and 8.0, respectively. Furthermore the uracil 3 position NH at δ 11.58 can also be seen to be very weak while the strong NH peak observed at δ 10.70 is good evidence for the existence of a dihydrouracil ring.[25] These values are in reference to external hexamethyldisiloxane (HMDS). The percentage uracil in the polymer as determined by integration (9%) is in good agreement with the ultraviolet data. The nmr spectrum is also consistent with the absence of pendant vinyl groups.

Infrared analysis (Figure 3a) of the polymer showed weak absorption at 808 cm^{-1} due to the loss of olefinic protons in the uracil rings. An increase in the intensity of this band was observed (Figure 3b) in the PVU which was prepared in chloroform at 61° with a benzoyl peroxide initiator. Ultraviolet analysis confirmed this result by indicating an increase in uracil rings to 18%.

The low extinction coefficient recently reported for the poly(1-vinyluracil) prepared by Pitha, Pitha, and Ts'o[22] is also consistent with substituted dihydrouracil formation and this may explain the incomplete base pairing that they observed with poly(adenylic acid), because dihydrouracil rings are known to be less effective in forming base pairs than uracils.[26] The PVU recently prepared by a Japanese group of chemists probably also contains substituted dihydrouracils.[27]

Structure of the Cyclopolymer. Although we have abundant physical evidence for the existence of substituted dihydro-

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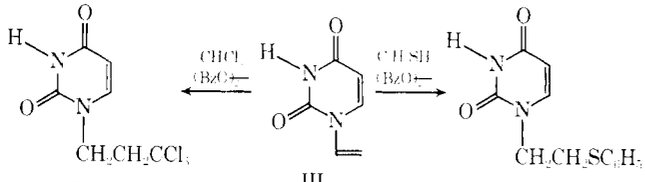
uracils in poly(1-vinyluracil), the spectral methods are unable to give us detailed information about the precise structure. The difficulty here was amplified by the myriad of possible structures which could fit the data. Some of these structures, neglecting stereoisomers, for which a mechanism of formation could be envisioned, are shown in Figure 4.

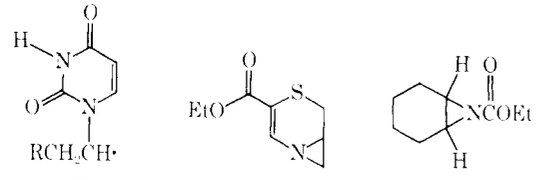
The possibility of uracil dimer formation leading to structure VIII as an explanation for our results did not seem likely to begin with, because uracil and thymine dimerization reactions require ultraviolet radiation at about 280 mμ to occur.[28] Dimerizations of this type have been shown to be reversible by irradiating the dimers at shorter[29] wavelengths. Irradiation of the polymer at 243 mμ for 8 hr resulted in no increase in absorption at 265 mμ, thereby eliminating structure VIII from consideration.

In the hope of trapping a monomeric cycloadduct that would be more amiable to structural analysis, the free radical additions of both thiophenol and chloroform to 1-vinyluracil were carried out. 1,4-Norbornadiene has been reported to form cycloadducts containing a three-membered ring in additions of this type.[30] In our case, the only products that could be isolated were those derived from normal addition to the 1-vinyl group. These results have demonstrated that the



XVII III XVIII

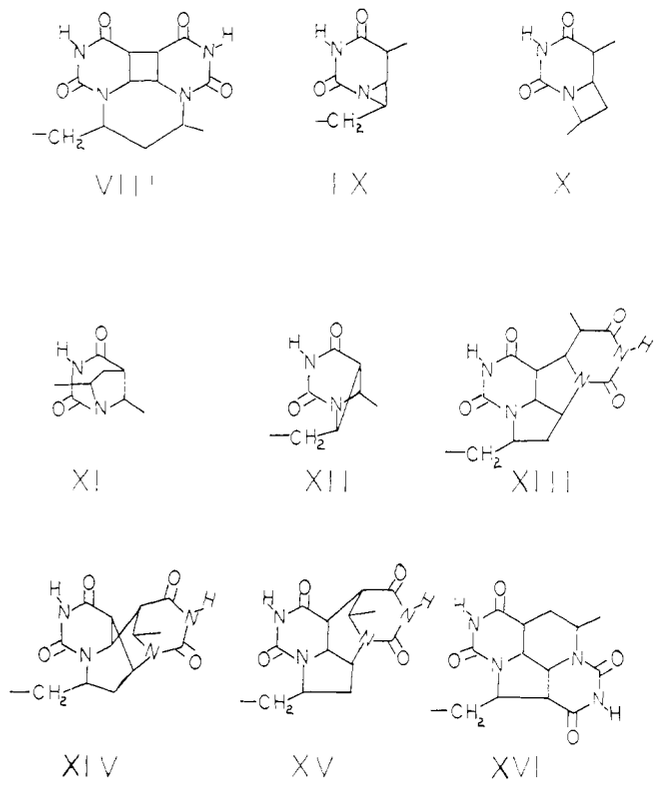
1-vinyl group is the double bond preferentially attacked by free radicals to produce radical XIX.



XIX XX XXI

The chain transfer constants of chloroform and thiophenol to XIX must be either greater than the apparent rate of formation of a cyclo free radical or the concentration of the monomer is too low for a cyclo dimer such as XIII to form. An example of the former situation has been observed in the addition of thiophenol to 1,4-norbornadiene.[31]

From the above results, structures X, XI, and XVI, which were derived from free radical attack at positions other than the 1-vinyl group, do not seem probable. The possibility of the eventual formation of XVI by the attack of XIX on the 5 position of III instead of at position 6 seems feasible from a localization energy[32] estimate, but it does not seem probable from a polarity point of view.[33,34] Support for the absence of XVI or the alternate structure resulting from attack on the



VIII IX X

XI XII XIII

XIV XV XVI

Figure 4. Possible structures of the cyclopolymer.

6 position has been obtained by observing the absence of pendant vinyl groups and a low percentage of uracil in the polymer. The rational for this is that a propagating free radical such as that derived from XVI, if it could form at all, would also be able to attack III at the 5 or 6 position and produce a new free radical which could not cyclopolymerize without increasing the percentage of uracil rings or which would leave pendant vinyl groups in the polymer.

A molecular model of XIX has shown, because of the planarity of the 1-nitrogen, that the free radical is too far away from the 5 positions for attack to take place. Structure XII therefore does not seem likely. Using similar arguments, molecular model studies suggest that structures XIV and XV are also improbable.

By a process of elimination the problem has been narrowed down to IX and XIII. Structure IX is an acylaziridine system which has not been reported in the literature, although a related structure, XX, has recently been prepared.[35]

Although we do not have Q or e values for III, a crude estimate for the values for the 1-vinyl and acrylic portions of the monomer can be obtained from the reported values for *N*-vinylpyrolidone ($Q = 0.14$, $e = -1.14$) and acrylamide ($Q = 1.18$, $e = 1.30$).[36] The opposite polarity here would favor cyclopolymerization of XIX to XXII. This same argument, however, can also be used to support the formation of a five-membered ring in the cyclization of XXIII to XXIV which would eventually lead to XIII (Figure 5). The latter mechanism can be considered to be a back-biting cyclopolymerization.

The nmr spectrum of the polymer (Figure 2a) at room temperature showed a broad peak at δ 4.8 with an area about twice that of the NH proton. At 148° this peak split into two signals at δ 4.87 and 4.56 probably due to motional

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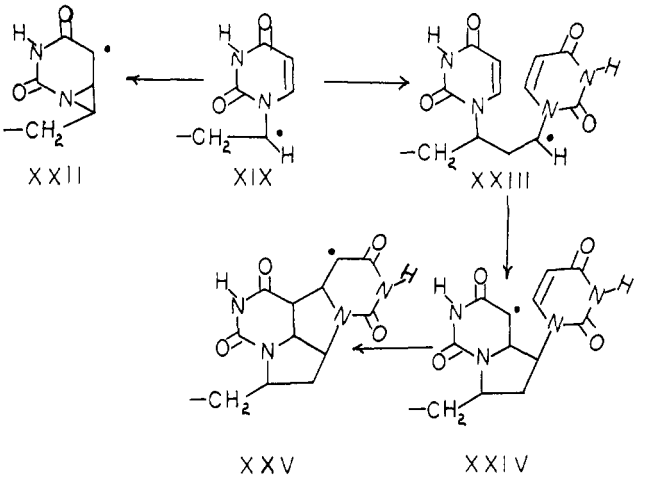


Figure 5. Cyclopolymerization mechanisms of 1-vinyluracil.

narrowing. The water peak disappeared under these conditions, and by subtracting out the DMSO-d_5 contribution an integration could be obtained. The assignment of the δ 4.87 and 4.56 signals to protons on the carbon α to the 1 nitrogen (2) and the higher field envelope to methylene protons (2) and protons α to the carbonyl group (1) was consistent with the integration. If IX is the correct structure then the δ 4.87 and 4.56 signals should correspond to the aziridine ring protons. These chemical shift values are at an anomalously low field because in dihydrouracil[37] the 6 protons are at δ 3.65 while in XXI[38] the aziridine ring protons are at δ 2.7 after correcting for HMDS as external reference. Unfortunately, we were not able to eliminate IX on this basis, because model studies of this polymer have revealed that both aziridine protons can easily lie in the plane of one of the carbonyl groups for each of the adjacent repeat units. The repeat units are about perpendicular to each other in this conformation. The magnetic anisotropy[39] of the carbonyl groups can very easily explain the deshielding observed for these aziridine protons. The deshielded proton in *N*-isopropylacrylamide[40] has been reported at δ 4.37 (HMDS), which is close to the chemical shift observed in poly(1-vinyluracil). The nmr spectrum (Figure 2a) is also consistent with structure XIII, because the 6 protons of similar fused-ring systems such as 1,1′-trimethylene bisthymine photodimer[41] and thymine photodimer[42] have been reported to occur at the low-field values of δ 4.30 and 4.44, respectively, in reference to HMDS. The nmr data are therefore unable to distinguish between IX and XIII.

Attempts have been made to distinguish between IX and XIII chemically, as it is well known that acylaziridines can isomerize to oxazolines under acidic, nucleophilic, and thermal conditions.[43] Models, however, have revealed that isomerization of IX to oxazolines would be impossible because of too much strain in these products. Nevertheless, the possibility of acid-catalyzed ring opening was attempted. After refluxing the polymer in concentrated hydrobromic acid for

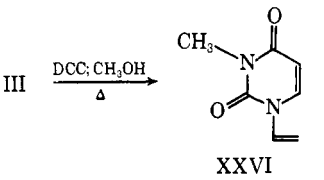
Figure 6. Infrared spectra of (a) poly(1-vinyluracil), (b) 1-ethyl-5-methyldihydrouracil, (c) poly(3-methyl-1-vinyluracil).

24 hr followed by precipitation from water, infrared spectroscopy could not detect any significant difference in the polymer. Similar results were obtained with hot concentrated sulfuric acid. This result favors structure XIII, but it is not completely conclusive because if protonation had occurred on either the 3 nitrogen or 4 oxygen[44] of IX, additional proton attack on the 2 oxygen or aziridine nitrogen would be inhibited by electrostatic repulsion.

The infrared CH stretching frequency for acylaziridine ring protons has been reported to occur at 3120 cm^{-1}.[45] Unfortunately the imide groups of dihydrouracil rings absorb in this region and prevent us from obtaining infrared evidence about the structure of the polymer. A comparison of the spectra of PVU and 1-ethyl-5-methyldihydrouracil in the CH stretching range (Figure 6a,b) points this out.

To circumvent this difficulty, 3-methyl-1-vinyluracil[16] (XXVI) was prepared by methylating III by the general procedure of Markiw and Canellakis.[46]

Polymerization of this monomer under the same conditions as used for III led to a polymer which had an infrared spec-



XXVI

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trum similar to PVU except in the 2700–3400-cm^{-1} region (Figure 6c). The absence of any absorption in the 3100-cm^{-1} vicinity strongly suggests that the polymer does not contain any acylaziridine rings. The strong absorption at higher wave numbers is probably due to adsorbed water. It therefore seems likely that structure XIII is the correct one.

Additional support for XIII has come from molecular model studies which have indicated that there is less strain in this structure and the fact that the 1 nitrogens can retain their planarity to a greater extent than in IX.

Summary and Conclusions

Abundant physical and chemical evidence has been presented for the existence of substituted dihydrouracil rings in free radically polymerized 1-vinyluracil. The result has been rationalized on the basis of the cyclopolymerization of a 1,4 diene which has one of its double bonds rigidly held in a ring.

Nuclear magnetic resonance and infrared spectroscopy of the polymer were not able to give detailed information about the structure.

Structure XIII formed *via* a back-biting cyclopolymerization mechanism is thought to be the correct structure for the cyclopolymer on the basis of a process of elimination and the following evidence.

1. The free radical additions of thiophenol and chloroform led to normal addition to the 1-vinyl group without cyclization.
2. The polymer did not contain any pendant vinyl groups and only 11% of the uracil rings were present.
3. Molecular model studies favor this structure from mechanistic, stereochemical, and ring strain points of view.
4. The infrared spectrum of poly(3-methyl-1-vinyluracil) showed the absence of acylaziridine ring protons.
5. The polymer was unchanged after treatment with hot hydrobromic acid and concentrated sulfuric acid.
6. Ultraviolet radiation of the polymer at 243 mμ did not cause an increase in absorption at 265 mμ.

Experimental Section

General. All melting points are corrected and analyses were carried out by Alfred Bernhardt Mikronanalytisches Laboratorium, Elbach Uber Engelskirchen, Germany. Nuclear magnetic resonance spectra were determined on a Varian HA 100 operating in the frequency mode which was locked on external HMDS for the polymer studies or internal TMS for compounds XVII and XVIII. A Cary 14 was used for ultraviolet measurements and Beckman IR 8 and IR 12 spectrophotometers were used for the infrared work. Ir spectra were determined in KBr pellets. Thin layer chromatography was carried out on microscope slides coated with Merck 254G silicic acid. Chromatograms were developed with chloroform–methanol mixtures and spots were detected with a short wavelength uv lamp.

Intrinsic viscosities were determined with a Cannon semimicro Ubbelhode viscometer. Differential thermal analysis and thermogravimetric analysis were carried out with Stone equipment.

1-(2-Chloroethyl)uracil (II). 2,4-Bis(trimethylsilyl)uracil[13] (100 g, 0.39 mol) was heated in a sealed tube with 370 ml of 1,2-dichloroethane at 100° for 2 days. At that time, the tube was opened and the contents were allowed to stir with 200 ml of methanol overnight at 25°. The mixture was taken to dryness on a rotating evaporator and then extracted with four 500-ml portions of boiling toluene. On cooling, a total of 6.09 g (9%) of 1-(2-chloroethyl)-uracil was obtained, mp 161–163°. Recrystallization from H_2O gave chromatographically pure material: mp 162–164°; uv max (pH 7 phosphate buffer) 264 mμ (ε 8650), 204 (7800) (by chlorination of 1-(2-hydroxyethyl)uracil, mp 164–167).[12] *Anal.* Calcd for $C_6H_7N_2O_2Cl$: C, 41.4; H, 4.02; N, 16.1; Cl, 20.1. Found: C, 41.24; H, 4.15; N, 16; Cl, 20.14. The nmr spectrum in DMSO-d_6 was as follows: 3 proton δ 11.30 (S, 1 H), 6 proton 7.70 (d, J_{56} = 8 Hz, 1 H); 5 proton 5.62 (q, J_{56} = 8 Hz, J_{35} = 2 Hz, 1 H), 1 and 2 ethyl protons 3.97 (ten lines, AA′BB′, 4 H).

β-Ethoxyacrylamide (VI). Anhydrous ammonia was bubbled through a solution of β-ethoxyacryloyl chloride[18] (2.60 g, 0.0194 mol) in dry ether (50 ml) at −25° under a nitrogen atmosphere. A thick white precipitate formed and after stirring for 10 min the excess ammonia was removed under vacuum. The residue was washed with warm chloroform and then the remaining solution was reduced to dryness. The white solid obtained was recrystallized from hot benzene yielding 1.52 g (68%) of colorless platelets of β-ethoxyacrylamide, mp 151–152°. *Anal.* Calcd for $C_5H_9NO_2$: C, 52.16; H, 7.87; N, 12.16. Found: C, 52.17; H, 8.41; N, 12.21.

***N*-β-Ethoxyacryloyl-*N*′-vinylurea (VII).** β-Ethoxyacrylamide (1.52 g, 0.0132 mol) and vinyl isocyanate[20] (0.95 g, 0.0138 mol) in toluene (60 ml) containing a trace of *m*-dinitrobenzene was heated at 100° for 24 hr in a sealed tube. After cooling to room temperature the reaction mixture was filtered and the solvent was removed under vacuum. The remaining residue was crystallized from ethanol yielding 1.72 g (74%) of *N*-β-ethoxyacryloyl-*N*′-vinylurea as white needles, mp 145–146°. *Anal.* Calcd for $C_8H_{12}N_2O_3$: C, 52.16; H, 6.56; N, 15.21. Found: C, 52.01; H, 6.74; N, 15.26.

1-Vinyluracil (III). a. 1-(2-Chloroethyl)uracil (6.0 g, 0.0344 mol) was stirred with potassium *tert*-butoxide (13 g) in 1200 ml of anhydrous THF for 2 days at 25°. The insoluble precipitate was filtered on a Teflon filter and then it was dissolved in 200 ml of 1:1 methanol–water for 2 days. After reducing the volume of the solution to 25 ml, 2 *N* HCl was added until pH 5 and then the solution was allowed to remain in the cold overnight. The collected product was dried under vacuum, dissolved in boiling toluene (300 ml), washed with Darco G-60, filtered, and then allowed to cool yielding 1.99 g (42%) of 1-vinyluracil as white crystals: mp 181–182°; uv max (0.1 *N* NaOH) 177 mμ (ε 9987), 222 (11,782), shoulder at 233 mμ. *Anal.* Calcd for $C_6H_6N_2O_2$: C, 52.16; H, 4.37; N, 20.28. Found: C, 52.33; H, 4.34; N, 20.32. Ir and nmr data are reported in ref 10.

b. *N*-β-Ethoxyacroyl-*N*′-vinylurea (0.2 g, 0.0011 mol) was heated on a steam bath with ethanol (3 ml) and 2 *N* sodium hydroxide (3 ml) for 1 hr. The mixture was neutralized to pH 6 with 2 *N* hydrochloric acid and then it was reduced to dryness under high vacuum. The residue was washed with hot chloroform which was immediately applied to a column of silicic acid. The column was eluted with 4% methanol in chloroform. After pooling the appropriate fractions and removing the solvent under reduced pressure, the remaining residue was crystallized from boiling toluene yielding 30 mg (20%) of white crystals of 1-vinyluracil: mp 178–180°; the product was identical with the material prepared in procedure a by mixture melting point and tlc.

1-Ethyluracil (IV). Vinyluracil (36 mg, 0.261 mmol) in 3 ml of water was injected into a Brown micro hydrogenator[14] containing 0.25 g of 10% palladium on carbon in 5 ml of methanol. Within 3 min the reduction was complete. The reaction mixture was filtered, reduced to dryness, and crystallized from hot toluene yielding 15 mg (48%) of 1-ethyluracil, mp 144–145°; the product was identical with authentic 1-ethyluracil[15] by mixture melting point and ir.

Poly(1-vinyluracil). a. 1-Vinyluracil (100 mg) was dissolved in 5 ml of distilled water and the solution was deaerated by passing through a rapid stream of nitrogen. After raising the solution to 95° under a nitrogen atmosphere, 0.122 ml of a freshly prepared 2.5×10^{-2} *M* potassium persulfate solution was added. Within 10 min the solution became milky. After 2 hr at 95° the milky suspension was cooled to room temperature. Enough 0.25 *N* sodium hydroxide was added to completely dissolve the polymer and then it was precipitated by the addition of 0.2 *N* hydrochloric acid. The polymer was washed with water, methanol, and ether and then it was dried at 100° (1 mm) for 24 hr yielding 72 mg (72%) of poly(1-vinyluracil) as a white powder. *Anal.* Calcd for $(C_6H_6N_2O_2)_n$: C, 52.16; H, 4.37; N, 20.28. Found: C, 52.04; H, 4.43; N, 20.11. Uv max (pH 7 phosphate buffer) 265 mμ (ε 1088); per cent uracil = 1088/9570 = 11.2%; $[\eta]^{25}$ =

0.14 (DMSO). The nmr and ir spectra are shown in Figures 2 and 3a.

b. 1-Vinyluracil (50 mg) was refluxed with 15 mg of benzoyl peroxide initiator in chloroform (10 ml) under nitrogen for 4 days. At the end of this time 21 mg (42%) of white poly(1-vinyluracil) had precipitated out: uv max 265 mμ (pH 7, phosphate buffer) (ε 1750), uracil = 1750/9750 = 18%. The ir spectrum is shown in Figure 3.

Addition of Thiophenol to 1-Vinyluracil. 1-Vinyluracil (100 mg, 0.724 mmol) was heated and stirred at 100° with 15 mg of benzoyl peroxide and 10 ml of thiophenol for 2 hr under a helium atmosphere. At this time the excess thiophenol was removed under reduced pressure and the remaining white residue was then triturated with *n*-hexane. Tlc of this residue indicated starting material and one product. After crystallization from boiling water, 45 mg (25%) of 1-(2-thiophenoxyethyl)uracil was obtained as white platelets, mp 132–133°. *Anal.* Calcd for $C_{12}H_{12}N_2O_2S$: C, 58.04; H, 4.87; N, 11.28; S, 12.91. Found: C, 57.88; H, 4.77; N, 11.18; S, 12.74. The nmr spectrum in acetone-d_6 was as follows: 6 proton δ 7.58 (d, J = 8 Hz, 1 H), phenyl protons 7.42 (m, 5 H), 5 proton 5.56 (d, J = 8 Hz, 1 H), 1 ethyl proton 4.4 (t, J = 7 Hz, 2 H), 2 ethyl protons 3.38 (t, J = 7 Hz, 2 H).

Addition of Chloroform to 1-Vinyluracil. 1-Vinyluracil (43 mg, 0.312 mmol) was refluxed with 40 mg of benzoyl peroxide in 150 ml of chloroform for 5 days under nitrogen. On the second and third days 10-mg portions of benzoyl peroxide were added. Under these conditions polymerization did not occur. The chloroform was removed under reduced pressure and the residue was triturated with hexane. After crystallization from methanol–water, 47 mg (57%) of 1-(2-trichloromethylethyl)uracil was obtained as white crystals, mp 174–176°. Tlc of this compound indicated that the product was homogeneous; the retention time was the same as that of the starting material. A mixture melting point determination, however, with 1-vinyluracil was depressed 34°. *Anal.* Calcd for $C_7H_7Cl_3N_2O_2$: C, 32.66; H, 2.72; N, 10.87. Found: C, 32.43; H, 2.85; N, 10.77. Mass spectrum showed *m/e* 257.9541 (empirical formula $C_7H_7Cl_3N_2O_2$).

The nmr spectrum in acetone-d_6 was as follows: 6 proton δ 7.64 (d, J_{56} = 8 Hz, 1 H), 5 proton 5.58 (d, J_{56} = 8 Hz, 1 H), 1 ethyl proton 4.42 (t, J = 7 Hz, 2 H), 2 ethyl protons 3.24 (t, J = 7 Hz, 2 H).

Poly(3-methyl-1-vinyluracil). The general methylation procedure of Markiw and Canellakis[46] was used. 1-Vinyluracil (100 mg, 0.725 mmol) was heated with dicyclohexylcarbodiimide (1 g, 4.9 mmol) and methanol (5 ml) at 80° for 24 hr in a sealed tube. The mixture was then kept at 4° for 12 hr and the white crystals which had formed were removed. The solution was reduced to dryness and the remaining residue was crystallized from cyclohexane two times after treatment with Darco G-60 absorbing charcoal yielding 32 mg (28%) of 3-methyl-1-vinyluracil as white needles melting at 95–96° (by the vinylation of 3-methyluracil, mp 95–97°).[16]

3-Methyl-1-vinyluracil (6 mg) was dissolved in 0.5 ml of distilled water and then it was polymerized under nitrogen at 95° with 0.01 ml of 2.5×10^{-2} M potassium persulfate. After 2 hr, the white precipitate which had formed was washed with methanol and then it was dried at 100° (1 mm) for 24 hr yielding 4 mg of poly(3-methyl-1-vinyluracil). The infrared spectrum of this polymer was very similar to that of PVU except in the 2700–3400-cm^{-1} vicinity. The infrared in this range is shown in Figure 6.

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Synthesis and Properties of Ethylene–Butene-1 Block Copolymers

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Abstract: A new method is described to introduce pure blocks of ethylene and ethylene–butene-1 into polymer systems. These polymers are prepared by the catalytic hydrogenation of 1,4-butadiene–(1,2- and 1,4-butadiene) copolymers. The properties of these polymer systems are discussed as a function of composition and degree of polymerization. This technique may be used to prepare ABA type thermoplastic elastomers.

The literature abounds with examples of copolymers of butene-1 and ethylene.[1–7] Ziegler catalysts such as vanadium tetrachloride combined with triethylaluminum produce macroblock block polymers when ethylene and butene-1 are present in equivalent amounts owing to the great difference in reactivity of ethylene and butene-1. With careful control of monomer concentration random ethylene–butene-1 polymers may be produced. Kontos, *et al.*,[8] have used a highly dispersed heterogeneous catalyst mixture of titanium tetrachloride with lithium aluminum alkyls to prepare living macromolecules. This technique may be used to prepare block copolymers of ethylene and butene-1 with a defined block sequence and number.

A new and more convenient synthesis of block copolymers of ethylene and butene-1 having a known, regular block sequence is described in this article, along with the effect of various block lengths and sequences on physical properties.

The ethylene–butene-1 block and random copolymers were prepared by the low-pressure catalytic hydrogenation of 1,4-butadiene–(1,2- and 1,4-butadiene) copolymers, *viz.*

(1) U. N. Gromova, *et al.*, *Polym. Sci. USSR*, **9** (5), 1250 (1967), and references cited therein.
(2) British Patent 1,049,345 (1966).
(3) Netherlands Patent 6,604,275 (1966).
(4) R. J. Kern, *et al.*, U. S. Patent 3,478,129 (1969), and references cited therein.
(5) A. A. Buniyat-Zade, *et al.*, *Dokl. Akad. Nauk Azerb. SSR*, **22** (5), 14 (1966), and references cited therein.
(6) H. J. Hagemeyer, *et al.*, U. S. Patent 3,304,292 (1967), and references cited therein.
(7) M. Iwamoto, *et al.*, U. S. Patent 3,336,277 (1967), and references cited therein.
(8) E. G. Kontos, *et al.*, *J. Polym. Sci.*, **61**, 69 (1962), and references cited therein.