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.*

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(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).

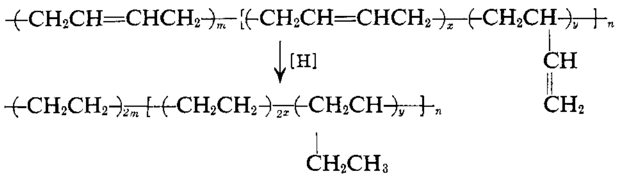
(4) R. J. Kern, *et al.*, U. S. Patent 3,478,129 (1969), and references cited therein.

(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.



$$\mathrm{-\!\!(CH_2CH{=}CHCH_2)_m\!-\![(CH_2CH{=}CHCH_2)_x\!-\!(CH_2\underset{\underset{CH_2}{\|}{CH}}{CH})_y]_n \xrightarrow{[H]} -\!\!(CH_2CH_2)_{2m}\!-\![(CH_2CH_2)_{2x}\!-\!(CH_2\underset{CH_2CH_3}{CH})_y]_n}$$

These hydrogenations were effected with the alkyllithium–transition metal octoate catalyst system previously described by Falk.[9] The requisite substrate polybutadienes were obtained by anionic polymerization in cyclohexane using *s*-butyllithium to initiate the reaction and controlled levels of tetramethylethylenediamine to provide the desired amount of 1,2 structure. Thus, anionic polymerization, first in cyclohexane to give living poly-1,4-butadiene having >90% 1,4 configuration, followed by polymerization of added monomer in the presence of one or more equivalents of tetramethylethylenediamine, afforded a two-block living polymer having 70% of the second block in the 1,2 configuration and 30% in the 1,4 form. Quenching of this with alcohol gave an AB block copolymer, while coupling with agents such as ethylene bromide formed a 1,4-butadiene–(1,2- and 1,4-butadiene)–1,4-butadiene ABA block copolymer. Hydrogenation produced ethylene–(ethylene, butene-1) and ethylene–(ethylene, butene-1)–ethylene AB and ABA block copolymers.

As indicated in Table I, the properties of hydrogenated poly-1,4-butadiene containing >90% 1,4 structure resemble those of polyethylene, giving a high tensile, orientable clear film. Increasing the 1,2 content or butene-1 component in a random fashion (entry 2) quickly produces a marked loss in tensile properties to give a soft rubbery characteristic which cannot be overcome by increased molecular weight alone (entry 3). Aggregating the ethylene–butene-1 portion into a separate block AB system (entry 4) appears to restore a portion of the strong, high tensile characteristics of the original ethylene while maintaining the rubbery nature of the ethylene–butene-1 copolymer. As indicated by the properties of a series of ethylene–(ethylene, butene-1) block copolymers, Table II, high ultimate tensile coupled with low tensile yield occurs between 55 and 85% polyethylene composition. The copolymers in this range also exhibited elastic recoveries between 85 and 93%, and can be considered thermoplastic elastomers. Some recently developed thermoplastic elastomers owe their properties to their ABA block structure.[10] These copolymers consist of rigid thermoplastic A blocks and soft, rubbery B segments, and exhibit behavior similar to that of cross-linked structures. Typical examples of such linear thermoplastic elastomers are those described by Morton[11] and Szwarc,[12] including polystyrene–poly-1,4-butadiene–polystyrene and polyethylene–poly(-ethylene, -propylene)–polyethylene.[13]

In our system, ABA block copolymers also exhibited thermoplastic elastomer behavior, as shown in Table III. At compositions from 55 to 85% ethylene, tough, clear rubbery materials were obtained, while above that range the materials begin to resemble the reduced anionic poly-1,4-butadiene reported in Table I.

TABLE I

PHYSICAL PROPERTIES OF ETHYLENE–BUTENE COPOLYMERS

Type	$\eta_{sp/c}$[c]	Tensile strength Yield, psi	Tensile strength Ultimate, psi	Elongation, %	Substrate[d] mol wt
>90% E		1260	3050	510	100,000
70 E-But[a]	1.84	220	430	770	120,000
60 E-But	2.66		610	1000	250,000
60 E-(E, But)[b]		640	2300	650	250,000

[a] 70 wt % ethylene, 30 wt % butene-1 random copolymer. [b] 60 E-(E, But) contains 60 wt % ethylene blocks and 40 wt % ethylene-butene-1 blocks. [c] 0.1 g/dl in decalin at 135°. [d] Calculated molecular weight of polybutadiene substrate.

TABLE II

PHYSICAL PROPERTIES OF ETHYLENE–(ETHYLENE, BUTENE-1) BLOCK COPOLYMERS

Composition	$\eta_{sp/c}$[a]	Tensile strength Yield, psi	Tensile strength Ultimate, psi	Elongation, %	Substrate mol wt
55 E–(E, But)			2100	800	120,000
66 E–(E, But)	1.73	710	1830	750	120,000
75 E–(E, But)		800	2550	740	120,000
60 E–(E, But)		640	2300	650	250,000
85 E–(E, But)		910	4100	550	250,000

[a] In decalin at 135°, 0.1 g/dl.

TABLE III

PHYSICAL PROPERTIES OF ETHYLENE–(ETHYLENE, BUTENE-1)–ETHYLENE BLOCK POLYMERS AS A FUNCTION OF COMPOSITION [a]

Composition	$\eta_{sp/c}$[d]	Tensile strength Yield, psi	Tensile strength Ultimate, psi	Elongation, %
45 E–(E, But)–E[b]	1.00	300	610	780
55 E–(E, But)–E	1.13	420	1010	940
66 E–(E, But)–E	1.06	670	1600	780
75 E–(E, But)–E	1.36	800	2010	770
85 E–(E, But)–E	1.22	970	2460	750
90 E–(E, But)–E		1200	3050	670
85 E–(E, But)–E[c]		1000	2970	730

[a] Substrate mol wt = 100,000. [b] E = ethylene; But = butene-1; 45 E–(E, But)–E contains 45% E A blocks. [c] Substrate mol wt = 250,000. [d] In decalin at 135°, 0.1 g/dl.

Comparing the data in Tables II and III, there would appear to be no advantage in the ABA system over the AB copolymer. If ABA block elastomers depend for their rubbery properties solely upon the aggregation of the rigid glassy domains which effectively act as network junctions, as suggested by Morton and others, then the properties exhibited by our AB systems is puzzling. While the ethylene–butene-1 portion of the AB structure might well associate sufficiently to complete the network effect, the lack of similar rubbery behavior in the random systems suggests otherwise. These observations suggest an interesting area for further study.

Molecular weight has a marked effect on physical properties. While molecular weights in the vicinity of 200,000 and up exhibit only modest changes in ultimate tensile strength,

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(9) J. C. Falk, *J. Org. Chem.*, in press.

(10) L. J. Fetters and M. Morton, *Macromolecules*, **2**, 453 (1969), and references cited therein.

(11) M. Morton and L. J. Fetters, *Macromol. Rev.*, **2**, 71 (1967).

(12) M. Szwarc, "Carbanions, Living Polymers and Electron Transfer Processes," Interscience, New York, N. Y., pp 73ff, 1968.

(13) H. L. Hassell and A. W. Shaw, South African Patent 665,994 (1966).

Table IV
Physical Properties of Ethylene–(Ethylene, Butene-1)–Ethylene Block Polymers as a Function of Molecular Weight [a]

$\eta_{sp/c}$[b]	Tensile strength Yield, psi	Ultimate, psi	Elongation, %	Substrate mol wt
1.01	640	1150	820	90,000
1.06	670	1600	780	120,000
1.67	660	2330	810	210,000
1.76	690	2510	800	240,000
1.95	670	2760	780	250,000

[a] Constant composition, 66% polyethylene A blocks. [b] In decalin at 135°, 0.1 g/dl.

these strength properties fall off rapidly with the molecular weight below that value (Table IV).[14]

We have described a new way to introduce blocks of ethylene and ethylene, butene-1 in a well-defined manner into polymer systems. This method involves the catalytic hydrogenation of 1,4-butadiene–(1,2- and 1,4-butadiene) block polymers. A useful feature of the technique of placing blocks of polyethylene and poly(-ethylene, -butene-1) in polymer systems is the preparation of ABA and AB type thermoplastic elastomers. The ethylene–(ethylene, butene-1)–ethylene and ethylene–(ethylene, butene-1) block polymers described in this paper exhibit thermoplastic elastomeric properties. With low yields, high ultimate tensile strength, good elongation, and elastic recovery, these polymers are consistent with the ASTM definition of elastomers:[15] "A substance that can be stretched at room temperature to at least twice its original length and, after having been stretched and the stress removed, returns with force to approximately its original length in a short time."

Experimental Section

Hydrogenation. Ethylene–(ethylene, butene-1) copolymers were prepared by the hydrogenation of 1,4-butadiene–(1,2- and 1,4-butadiene) copolymers according to the method of Falk.[9] A 1,4-butadiene–(1,2- and 1,4-butadiene)–1,4-butadiene block copolymer, 20.0 g, was dissolved in 1500 ml of cyclohexane and placed with 0.3 mol % of cobalt octoate–*n*-butyllithium catalyst having a lithium–cobalt ratio of 2.2:1 in a 2-l. reactor thermostated at 50°. Hydrogen was bubbled through the reactor at a constant hydrogen pressure of 50 psi throughout the hydrogenation. The reaction was carried out until the infrared spectrum of an aliquot was free of absorption due to butadiene unsaturation, a 20-min reaction time. The polymer solvent mixture was washed with dilute aqueous acid to remove catalyst residue, then precipitated in 2-propanol and dried at 60° under vacuum.

Synthesis. A solution of 15 g (0.28 mol) of butadiene in 700 ml of cyclohexane under a dry nitrogen atmosphere was treated with 0.3 mmol of *s*-butyllithium. The reaction mixture was kept at 50° for 16 hr. Dry, freshly distilled tetramethylethylenediamine, 0.6 mmol, was added, followed by 15 g (0.28 mol) of butadiene. After an additional 16 hr at 50° 0.15 mmol of ethylene bromide was added and the reaction was kept at 50° for 4 hr. A 1,4-butadiene–(1,2- and 1,4-butadiene)–1,4-butadiene block copolymer was produced. Infrared analysis showed the microstructure of the A block to contain 43% cis-1,4, 49% trans-1,4, and 8% 1,2 structure. The B block contains 70% 1,2 and 30% cis- and trans-1,4 structures. Prior to hydrogenation the copolymer was precipitated in 2-propanol, dried at 60° under vacuum, and redissolved in cyclohexane.

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(14) Molecular weights indicated throughout the paper are those calculated for the substrate polybutadiene. Lack of suitable methods prevented our ascertaining whether degradation occurred with these mild hydrogenations. Hydrogenations using the same catalyst in analogous systems in these laboratories show little degradation. The $\eta_{sp/c}$ values, measured on the ethylene–butene-1 copolymers, may reflect only a trend.

(15) *Amer. Soc. Test. Mater., Spec. Tech. Publ.*, No. **184**, 42 (1956).