Formation of Linear Polymers from Diene Monomers by a Cyclic Polymerization Mechanism. IV. Synthesis and Polymerization Studies of Some Doubly-Unsaturated, Unsymmetrical Monomers[1]

MARTIN D. BARNETT[2a,b] AND GEORGE B. BUTLER

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Current interest in the polymerization of symmetrical dienes by an alternating intramolecular-intermolecular mechanism has led to extensive studies in this field.[3] Previous work[3] in these Laboratories has successfully extended the scope of this reaction to unsymmetrical dienes. We now wish to report the synthesis and results of the polymerization studies of a number of unsaturated derivatives of crotyl and vinylacetic acid, additional examples of unsymmetrical, doubly-unsaturated monomers.

EXPERIMENTAL[4]

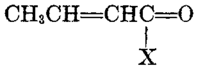
Monomers. The *esters of crotonic acid* were prepared by refluxing a benzene solution (200 ml.) of *trans*-crotonic acid (0.5 mol.), the appropriate alcohol (0.55 mol.), and *p*-toluenesulfonic acid (1.0 g.) under a Dean-Stark trap until water evolution ceased (*ca.* 24 hr.). The reaction mixtures were worked up as previously described.[3]

The *esters of vinylacetic acid* were prepared by the dropwise addition of vinylacetyl chloride[5] (0.2 mol.) to a stirred solution of the appropriate alcohol (0.22 mol.) and pyridine (0.21 mol.) in 125 ml. of dry ether. The temperature of the reaction mixture was maintained at 0–5° throughout the addition, after which the cooling bath was removed and the mixture stirred an additional 4 hr. One hundred milliliters of water was added, and the ether layer washed with saturated sodium bicarbonate solution, water, and dried over anhydrous sodium sulfate. Distillation afforded the desired ester.

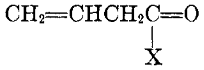
N-Allylcrotonamide was prepared by the dropwise addition of a solution of 0.5 mol. of crotonyl chloride in 50 ml. of dry ethylene dichloride to a cooled (0°), stirred solution of 1.01 mol. of allyl amine in 400 ml. of dry ethylene dichloride.[6] When addition was complete the mixture was allowed to warm to room temperature and stirred overnight. The work-up was identical with that of the above vinylacetates.

TABLE I

PHYSICAL PROPERTIES OF MONOMERS



$CH_3CH{=}CH\underset{\overset{|}{X}}{C}{=}O$ (I)



$CH_2{=}CHCH_2\underset{\overset{|}{X}}{C}{=}O$ (II)

Compound	Yield, %	B.P., °/Mm.	n_D^{22}	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
Ia. X = $-OCH_2CH{=}CH_2$[a]	—	63–64°/22	1.4452	—	—	—	—
Ib. X = $-OCH_2CH{=}CHCH_3$[b]	33	84–86°/22	1.4484	68.54	68.77	8.63	8.77
Ic. X = $-OCH_2\overset{\overset{CH_3}{|}}{C}{=}CH_2$	41	77.3–77.5°/22	1.4491	68.54	68.49	8.63	8.79
Id. X = $-OCH_2C{\equiv}CH$	37	79.5–80.5°/25	1.4583	67.73	67.53	6.41	6.50
Ie. X = $-NCH_2CH{=}CH_2$[c]	83	90–91°/0.8	1.4911	67.16	67.32	8.86	8.91
IIa. X = $-OCH_2CH{=}CH_2$	48	58–58.5°/27	1.4313	66.64	66.76	7.99	8.15
IIb. X = $-OCH_2CH{=}CHCH_3$	56	78–79°/27	1.4374	68.54	68.25	8.63	8.81
IIc. X = $-OCH_2\overset{\overset{CH_3}{|}}{C}{=}CH_2$	53	73–74°/27	1.4351	68.54	68.42	8.63	8.88

[a] V. P. Golendeev, *J. Gen. Chem.* (*U.S.S.R.*), **10,** 1408 (1940) [*Chem. Abstr.*, **35,** 3607[6] (1941)] reports b.p. 88–89°/70 mm., n_D^{20} 1.4465. [b] F. C. Frostick, Jr., B.Phillips, and P. S. Starcher, *J. Am. Chem. Soc.*, **81,** 3350 (1959), report b.p. 85–87°/25 mm., n_D^{30} 1.4495. [c] N: Calcd., 11.19. Found, 11.15.

The infrared spectra (liquid films) of the monomers were consistent with their assigned structures. Physical data are recorded in Table I.

Polymerizations were carried out in bulk under dry nitrogen using 5–10 g. samples of monomer and 2% by weight of the appropriate initiator [benzoyl peroxide or azobisisobutyronitrile]. The solid polymers were isolated and purified as previously described.[3] Benzoyl peroxide-initiated polymerizations were run at 100°; those using azobisisobutyronitrile were maintained at 75°. Data concerning the polymerizations is summarized in Table II.

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[1] This research was supported by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command, under Contract Number AF 18(603)-116. Reproduction in whole or in part is permitted for any purpose of the United States Government.

[2a] Post-doctoral fellow, 1958–1959; (b) Present address: Department of Chemistry, Marshall College, Huntington, W. Va.

[3] The previous paper in this series [M. D. Barnett, A. Crawshaw, and G. B. Butler, *J. Am. Chem. Soc.*, **81,** 5946 (1959)] contains many pertinent references.

[4] All boiling points are uncorrected. Infrared spectra were recorded using a Perkin-Elmer Model 21 double beam spectrophotometer. Analyses were carried out by Galbraith Laboratories, Knoxville, Tenn., or by Weiler and Strauss, Oxford, England.

[5] G. H. Jeffery and A. J. Vogel, *J. Chem. Soc.*, 658 (1948).

[6] W. S. Weaver and W. M. Whaley, *J. Am. Chem. Soc.*, **69,** 515 (1947).

TABLE II

POLYMERIZATION STUDIES

Monomer	Polymer (Approximate Values) % Residual Alcohol Bond	% Residual Acid Bond	% Cyclization	Approximate % Conversion	Gel Time (hr.)	Inherent Viscosity (g. polymer/100 ml. solution)	Observations
Ia[a]	15	60	25	10	110	0.046 (0.198)	—
Ib	—	—	—	—	—	—	No polymer with 2% Bz_2O_2[d] at 100° for 45 days or 2% AIBN[e] at 75° for 14 days
Ic[b]	11	58	31	10	[c]	0.039 (0.207)	—
Id	—	—	—	—	—	—	No solid polymer with 2% Bz_2O_2 at 100° for 29 days
Ie	—	—	—	—	—	—	No polymer with 2% Bz_2O_2 at 100° for 14 days or 2% AIBN at 75° for 14 days
IIa	—	—	—	—	—	—	No solid polymer with 2% Bz_2O_2 at 100° for 22 days or 2% AIBN at 25° for 11 days
IIb	—	—	—	—	—	—	No polymer with 2% Bz_2O_2 at 100° for 25 days or 2% AIBN at 75° for 12 days
IIc	—	—	—	—	—	—	No solid polymer with 2% Bz_2O_2 at 100° for 25 days or 2% AIBN at 75° for 12 days

[a] Calcd. for $(C_7H_{10}O_2)_n$: C, 66.64; H, 7.99. Found: C, 66.37; H, 7.90. [b] Calcd. for $(C_8H_{12}O_2)_n$: C, 68.54; H, 8.63. Found: C, 68.37; H, 8.29. [c] No gelation after 32 days at 100° using 2% Bz_2O_2. [d] Benzoyl peroxide. [e] Azobisisobutyronitrile.

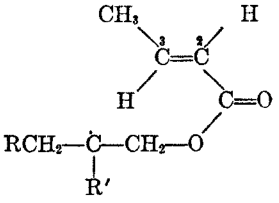
Residual unsaturation was determined as previously described[3] (Table II).

Inherent viscosity measurements were carried out in glacial acetic acid at 30.0° using a modified Ubbelohde viscometer (Table II).

Results and discussion. As indicated in Table II only allyl crotonate (Ia) and β-methallyl crotonate (Ic) gave solid, titratable polymers. Crotyl crotonate (Ib), crotyl vinylacetate (IIb) and *N*-allylcrotonamide (Ie) gave no polymeric material; allyl vinylacetate (IIa), β-methallyl vinylacetate (IIc) and propargyl crotonate (Id) afforded only viscous oils which resisted crystallization.

The relatively low degree of cyclization in poly(allyl crotonate) and poly(β-methallyl crotonate) is not surprising in view of the great difference in reactivities between the alcohol and acid bonds. This effect of differences in bond reactivities as reflected in linear *vs.* cyclopolymerization has been noted earlier.[3]

In addition to the anticipated absorption in the C=C stretching (1640–1655 cm.$^{-1}$) and carbonyl (1725–1740 cm.$^{-1}$) regions the infrared spectra (solid film from carbon tetrachloride) of the solid polymers showed a strong band at 1770–1772 cm.$^{-1}$ characteristic of a 5-membered lactone ring.[7] These findings were surprising, for although molecular models indicated somewhat less steric hindrance to attack of the initially-formed free radical at C_2 of the acid (5-membered lactone ring) rather than at C_3 (6-membered lactone ring), attack at C_3 should be favored by virtue of the resonance-stabilized radical formed at C_2.



R′ = —H, —CH₃

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF FLORIDA
GAINESVILLE, FLA.

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[7] H. K. Hall and R. Zbinden, *J. Am. Chem. Soc.*, 80, 6428 (1958).

Preparation of Hexaphenylcyclotrisiloxane by the Reaction of Diphenyldichlorosilane with Zinc Oxide

TOSHIO TAKIGUCHI, MASARU SAKURAI, TAKESHI KISHI
JUNJI ICHIMURA, AND YASUICHI IIZUKA

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In recent papers,[1] the senior author has described some methods which involve direct synthesis of

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[1] T. Takiguchi, *J. Org. Chem.*, 23, 1216 (1958); T. Takiguchi, *J. Chem. Soc. Japan* (*Ind. Chem. Sect.*), 61, 478 (1958); T. Takiguchi, *J. Chem. Soc. Japan* (*Ind. Chem. Sect.*), 62, 148 (1959); T. Takiguchi, *J. Org. Chem.*, 24, 861 (1959).