

*Anal.* Calcd. for  $C_{27}H_{46}$ : C, 87.49; H, 12.51. Found: C, 87.65; H, 12.34.

**Hydroxylation and Subsequent Acetylation of  $\Delta^{16(17)}$ -Cholestene (XV).**—As in the prior preparation of XIb, 50 mg. of  $\Delta^{16(17)}$ -cholestene and 100 mg. of osmium tetroxide were allowed to stand at room temperature overnight. The crystalline glycol thus obtained was acetylated (acetic anhydride-pyridine, steam bath, 2 hr.). Careful chromatography of the crystalline acetate yielded 44 mg. of the **hydroxy acetate (XVI)** as the only product, m.p. 174–175°,  $[\alpha]_D -47^\circ$ ;  $\nu^{CS_2}$  1745 (s, acetate) and 3571 (hydroxyl)  $cm^{-1}$ . The infrared spectra of XIb and XVI were different.

*Anal.* Calcd. for  $C_{29}H_{50}O_3$ : C, 77.97; H, 11.28. Found: C, 78.26; H, 11.33.

**17-Iso,20-isocholestane (IXa).**—A mixture of 0.3 g. of  $\Delta^{16(17)}$ -20-isocholestene (IVa), 1.0 g. of 10% palladium on charcoal, 25 ml. of ethyl acetate, and 10 ml. of acetic acid was shaken with hydrogen at room temperature and pressure for 2 hr. The crystalline residue obtained from the reaction gave 250 mg. of plates, m.p. 98–99°. A second recrystallization from ether-methanol gave 235 mg. of IXa, m.p. 99.5–100.5°,  $[\alpha]_D -2^\circ$ , negative tetranitromethane test.

*Anal.* Calcd. for  $C_{27}H_{48}$ : C, 87.02; H, 12.98. Found: C, 87.10; H, 12.71.

Hydrogenation of  $\Delta^{16(17)}$ -cholestene (XV) under similar conditions gave cholestane (XVII), m.p. 78–79°. Mixture melting point with an authentic sample of cholestane showed no depression. The compounds had identical infrared spectra.

The Raney nickel reduction of the 17-iso,20-isocholestan-16-one 16-ethylenethioketal (VIIb) afforded plates from ether-methanol, m.p. 76–78°,  $[\alpha]_D +4^\circ$ . The infrared spectra of this material and the substance obtained from catalytic hydrogenation of IVa were different.

**17-Iso,20-isocholestan-3 $\beta$ -ol (IXb).**—A mixture of 100 mg. of  $\Delta^{16(17)}$ -20-isocholestan-3 $\beta$ -ol (IVb), 50 ml. of ethyl acetate, 5 ml. of acetic acid, and 50 mg. of platinum oxide was shaken with hydrogen at room temperature and pressure. The crystalline residue crystallized from ethanol gave needles, m.p. 160–163°. The material recrystallized twice from ethanol gave 60 mg. of needles, m.p. 165–166°,  $[\alpha]_D -6.6^\circ$ . Mixture melting point with 20-isocholestan-3 $\beta$ -ol (m.p. 160–161°)<sup>15</sup> showed a depression, m.p. 130–137°.

*Anal.* Calcd. for  $C_{27}H_{48}O$ : C, 83.43; H, 12.45. Found: C, 83.70; H, 12.22.

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## Telomerization by Free-Radical Mercaptan Chain Transfer. II. Telomers of Acrylate Esters with Simple Thiols<sup>1,2</sup>

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Preparation and characterization of ten telomers formed from acrylate esters in reactions with methyl and ethyl mercaptans are reported. Determination of the first three telomerization chain transfer constants and the polymerization chain transfer constant for the methyl acrylate-ethanethiol system is also described. The two-unit transfer constant is about equal to the polymerization constant, but the three-unit constant is substantially higher than either. This suggests that a reactivity minimum exists for the three-unit radical such as has been reported for bromotrichloromethane telomers. A possible explanation is suggested.

Studies of telomerization of several monomers with bromotrichloromethane<sup>3</sup> have yielded evidence for an unexplained reactivity minimum in radical chains three or four units long. Propagation rate constants ( $k_p$ ) are reported to be significantly lower for these lengths than for shorter or longer chains. Rate constants for chain transfer ( $k_d$ ) are much less reduced; hence the Mayo chain transfer constants ( $C_n = k_d/k_p$ ) show a corresponding maximum.

Some exchange reaction or interaction involving the chain end seems implied by these findings, but its nature is still obscure. Kirkham and Robb<sup>3b</sup> suggested a "semibond" interaction between a terminal chlorine atom and the radical-bearing carbon. In three- and four-unit chains these are eight and ten atoms apart respectively, which are usually considered improbable

intervals for maximum direct interaction. However, there is some uncertainty about the chain sizes involved since the experiments on which these results are based do not involve quantitative separation of telomer products.

Kharasch and Fuchs<sup>4</sup> showed that methyl acrylate yields mixtures of volatile telomers when it reacts with ethanethiol in the presence of a free-radical initiator; hence acrylate esters and low molecular weight thiols appear to be promising systems for telomerization studies involving discrete separations of products by gas chromatography. This paper reports identification and characterization of ten acrylate ester telomers with methyl and ethyl mercaptans. Determination of several chain transfer constants in the methyl acrylate-ethanethiol system, which show some evidence for a reactivity minimum, also are described.

A procedure for obtaining telomer chain transfer constants similar to that described by Scott and Wang<sup>2</sup> was employed. This has the advantage that only ratios of successive telomer concentrations formed at low conversion and varying monomer to thiol ratios need to be measured. Chances for experimental errors are thereby minimized. The polymerization chain transfer

(1) (a) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research; (b) presented in part at the 144th National meeting of the American Chemical Society, Division of Polymer Chemistry, Los Angeles, Calif., April, 1963.

(2) Paper I in this series, G. P. Scott and J. C. Wang, *J. Org. Chem.*, **28**, 1314 (1963).

(3) (a) J. C. Robb and E. Senogles, *Trans. Faraday Soc.*, **58**, 708 (1962); (b) W. J. Kirkham and J. C. Robb, *ibid.*, **57**, 1757 (1961); (c) J. C. Robb and D. Vofsi, *ibid.*, **55**, 558 (1959); (d) W. I. Bengough and R. A. M. Thompson, *ibid.*, **57**, 1928 (1961); (e) **56**, 407 (1960).

(4) M. S. Kharasch and C. F. Fuchs, *J. Org. Chem.*, **13**, 97 (1948).

TABLE I  
 ACRYLATE ESTER TELOMERS AND DERIVATIVES

	Physical <sup>a</sup> constants	Formula	Analysis, <sup>b</sup> %	
			Calcd.	Found
Methyl acrylate-methanethiol				
One-unit telomer <sup>c</sup>	B.p. 118–119° (2 mm.) $n_{25}^D$ 1.4668	C <sub>5</sub> H <sub>10</sub> O <sub>2</sub> S	<i>h</i>	
One-unit sulfone	M.p. 96.5°	C <sub>5</sub> H <sub>10</sub> O <sub>3</sub> S	<i>h</i>	
Two-unit telomer <sup>d</sup>	B.p. 158–160° (2 mm.) $n_{25}^D$ 1.4759	C <sub>9</sub> H <sub>16</sub> O <sub>4</sub> S	C 49.05 H 7.27	49.20 7.63
Two-unit sulfone	M.p. 71.0–72.0°	C <sub>9</sub> H <sub>16</sub> O <sub>5</sub> S	C 42.46 H 6.35 S 12.69	42.48 6.95 12.70
Methyl acrylate-ethanethiol				
One-unit telomer <sup>e</sup>	B.p. 73.0–75.0° (1.5 mm.) $n_{25}^D$ 1.4589	C <sub>6</sub> H <sub>12</sub> O <sub>2</sub> S	C 48.62 H 8.16	48.67 8.00
One-unit acid sulfone <sup>f</sup>	M.p. 115–116°	C <sub>6</sub> H <sub>10</sub> O <sub>4</sub> S	C 36.13 H 6.07 S 19.29	36.25 6.23 19.40
One-unit benzylamide	M.p. 50–51°	C <sub>12</sub> H <sub>17</sub> ONS	C 64.53 H 7.67 S 14.36	64.67 7.88 14.53
Two-unit telomer <sup>g</sup>	B.p. 110–112° (0.3 mm.) $n_{25}^D$ 1.4664	C <sub>10</sub> H <sub>18</sub> O <sub>4</sub> S	C 51.26 H 7.74	51.45 7.71
Two-unit benzylamide	M.p. 138–139°	C <sub>22</sub> H <sub>28</sub> O <sub>2</sub> N <sub>2</sub> S	C 68.71 H 7.34 S 8.34	68.50 7.12 8.10
Three-unit telomer <sup>g</sup>	B.p. 164–166° (0.2 mm.) $n_{25}^D$ 1.4692	C <sub>14</sub> H <sub>24</sub> O <sub>6</sub> S	C 52.48 H 7.55 S 10.01	52.42 7.46 9.87
Ethyl acrylate-ethanethiol				
One-unit telomer <sup>e</sup>	B.p. 53–55° (0.3 mm.) $n_{27}^D$ 1.4543	C <sub>7</sub> H <sub>14</sub> O <sub>2</sub> S	C 51.82 H 8.70	52.00 8.88
Two-unit telomer <sup>f</sup>	B.p. 123–125° (0.5 mm.) $n_{27}^D$ 1.4593	C <sub>12</sub> H <sub>22</sub> O <sub>4</sub> S	C 54.93 H 8.12	54.77 8.48
Three-unit telomer <sup>g</sup>	B.p. 177–179° (0.2 mm.) $n_{27}^D$ 1.4615	C <sub>17</sub> H <sub>30</sub> O <sub>6</sub> S	C 56.33 H 8.35 S 8.85	56.39 8.49 8.95
Isopropyl acrylate-ethanethiol				
One-unit telomer <sup>e</sup>	B.p. 41–43 (0.4 mm.) $n_{25}^D$ 1.4517	C <sub>8</sub> H <sub>16</sub> O <sub>2</sub> S	C 54.51 H 9.15	54.49 9.18
Two-unit telomer <sup>f</sup>	B.p. 101–103° (0.3 mm.) $n_{25}^D$ 1.4517	C <sub>14</sub> H <sub>26</sub> O <sub>4</sub> S	C 57.90 H 9.02	58.24 9.12

<sup>a</sup> Melting points and boiling points are uncorrected. <sup>b</sup> Microanalyses are by Galbraith Laboratories, Knoxville, Tenn., and Mikrotech Laboratories, Skokie, Ill. <sup>c</sup> 3-Thiomethylpropionic acid methyl ester. <sup>d</sup> 2-Thiomethylethylglutaric acid dimethyl ester. <sup>e</sup> 3-Thioethylpropionic acid methyl, ethyl, and isopropyl esters. <sup>f</sup> 2-Thioethylmethylglutaric acid dimethyl, diethyl, and diisopropyl esters. <sup>g</sup> 6-Thioethyl-1,3,5-hexanetricarboxylic acid trimethyl and triethyl esters. <sup>h</sup> Sulfone m.p. 94.0–94.6° reported; A. J. Haagen-Smit, J. G. Kirchner, C. L. Deasy and A. N. Prater, *J. Am. Chem. Soc.*, **67**, 1651 (1945). <sup>i</sup> Cf. ref. 4.

constant  $C_{\infty}$  was determined by the method of Gregg, Alderman, and Mayo.<sup>5</sup>

### Experimental

**Materials.**—Commercial grade thiols and acrylate esters were redistilled twice just prior to each experiment; fractions boiling over a 1° range were used. Other materials of best commercial grades were used without further purification.

**Preparation and Isolation of Telomers.**—Mixtures of ester and thiol in mole ratios (ester/thiol) of 0.9 to 1.3 were sealed with 0.1 to 0.5 mole % of azobisisobutyronitrile (AIBN) in 30-ml. Pyrex tubes and heated at 50° for periods of 2.0 to 24 hr. After removing unchanged thiol and ester with a water aspirator, mixtures were fractionated at low pressures. Major fractions were redistilled and the purity of the resulting samples checked by gas chromatography. Additional distillations were carried out when necessary.

**Sulfones.**—In each case esters were treated with excess 30% hydrogen peroxide in glacial acetic acid. Attempts were made to crystallize the resulting oils from various solvents. Ester sulfones formed from the methanethiol telomers. The one-unit

sulfones from the ethanethiol telomers hydrolyzed to the acid sulfone before crystallizing. The higher ethanethiol telomers gave only oils.

**Benzylamides.**—A mixture of methyl acrylate-ethanethiol one-unit telomer (1.0 g.), 3.0 ml. of benzylamine, and 0.1 g. of powdered ammonium chloride was heated for 1 hr. in an oil bath under a gentle reflux. The resulting mixture was washed with water and crystallized in the presence of a little hydrochloric acid. The product was recrystallized twice from a mixture of petroleum ether (b.p. 70–90°) and a little ethyl acetate.

Preparation of the benzylamide from the two-unit telomer was carried out in the same way except that the relative amount of benzylamine was twice as great. The yield of this amide was small.

**Determination of Telomer Chain Transfer Constants.**—Mixtures of methyl acrylate and ethanethiol of varying mole ratios totaling 4 to 6 g. containing AIBN (0.1–0.4 mole % of the thiol) were sealed in acid-washed, nitrogen-filled 8-ml. Pyrex tubes and heated 0.5 to 4.5 hr. in a constant temperature bath at 50.0 ± 0.5°. Gas chromatograms of the resulting mixtures were run at 100° on a 0.5 in. × 5 ft. column containing 60/80 firebrick coated with 20% GE-SF-96 silicone oil using methanol as an internal standard to determine per cent of methyl acrylate consumed. If more than 10% had been consumed, the run was rejected. The column was then heated to 250° and several chromatograms

(5) R. A. Gregg, D. M. Alderman, and F. R. Mayo, *J. Am. Chem. Soc.*, **70**, 3740 (1948).

run, interspersed with chromatograms of prepared standard mixtures of one- and two-unit telomers similar in ratio to the sample, to calculate the one- to two-unit telomer ratios formed in each reaction. Relatively large injections (up to 60  $\mu$ l.) were required for each chromatogram owing to the high per cent of starting material present. Reaction mixtures were stored in Dry Ice and acetone to avoid further reaction and analyzed as soon as possible.

In runs used for measurement of ratios of two- to three-unit telomers, the same procedure was followed except that a 0.25 in.  $\times$  15 ft. column containing 60/80 firebrick coated with 20% SE-30 silicone oil was used and the column temperature was raised to 300°.

**Determination of Polymerization Chain Transfer Constants.**—Mixtures of methyl acrylate containing 0.0145 mole of ethanethiol and 0.00029 mole of AIBN per mole of ester were sealed in 30-ml. acid-washed, nitrogen-filled Pyrex tubes and heated in a constant temperature bath at 50.0  $\pm$  0.5° until the polymerization had proceeded to the desired extent as indicated by an increase in viscosity of the mixture. Tubes were then stored at -20° until they could be analyzed for thiol and ester remaining.

The per cent of ethanethiol remaining was measured by amperometric titration.<sup>6</sup> To avoid appreciable interference by methyl acrylate, the following procedure was used. Aliquots of only 0.50 ml. were injected into a titration cell containing 100 ml. of methanol, 2 ml. of 5 M ammonium nitrate, and 1.5 ml. of 4 M ammonium hydroxide vigorously stirred by a magnetic stirrer (as well as the rotating platinum electrode) in an ice bath maintaining the temperature below 10°. Titration with 0.0035 N silver nitrate was carried out as rapidly as possible guided by a rough preliminary titration to determine the approximate end point.

Determination of the per cent methyl acrylate remaining was carried out by gas chromatography as described in the preceding section except that acetone was used as the internal standard instead of methanol.

## Results

**Telomers and Derivatives.**—Properties of telomers and derivatives prepared so far are listed in Table I.

All telomers were colorless liquids; the increase in viscosity for the higher telomers was very noticeable. Attempts to prepare satisfactory solid derivatives to characterize these products have been only partially successful because of the reluctance of many of the usual products to crystallize. The three-unit telomers were presumably mixtures of isotactic and syndiotactic diastereomers (two *dl* pairs); however, in attempts to separate these forms of the methyl acrylate three-unit telomer on a 15-ft. column, it behaved like a pure compound. Telomers higher than three-unit have not been separated owing to their high boiling points.

These products are quite stable. Heating the one-unit methyl acrylate telomer 24 hr. at 50° in the presence of 1 mole % AIBN (as described in ref. 2) indicated that less than 1% had decomposed to give back methyl acrylate and ethanethiol. No decomposition at all was noted in the two-unit telomer under the same conditions.

**Chain Transfer Constants.**—Data for determination of telomer chain transfer constants are listed in Table II. The telomer ratios at less than 10% conversion are assumed<sup>2</sup> to closely approximate the left side of eq. 1

$$\frac{d[B - M_n - A]}{d[B - M_{n+1} - A]} = C_n[AB]/[M] + C_n/C_{n+1} \quad (1)$$

where [AB] and [M] are the monomer and thiol concentrations, respectively, and  $C_n$  and  $C_{n+1}$  refer to  $C_1$  and  $C_2$ , or  $C_2$  and  $C_3$ . The linear slopes of one- to two-

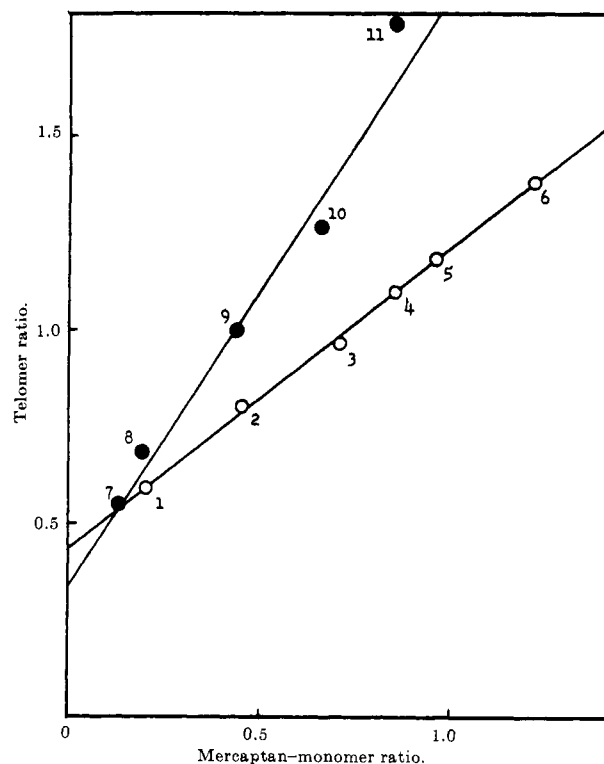


Fig. 1.—One-unit to two-unit telomer mole ratio, ○, and two-unit to three-unit telomer mole ratio, ●, plotted against ethanethiol to methyl acrylate mole ratio.

unit telomer ratios (runs 1 through 6) and two- to three-unit telomer ratios (runs 7 through 11) obtained by least squares calculations are equal to  $C_1$  and  $C_2$ , respectively (see Fig. 1). The intercepts equal  $C_1/C_2$  and  $C_2/C_3$ . From these a check value for  $C_2$  and a value for  $C_3$  are calculated.

TABLE II  
DATA FOR CALCULATION OF TELOMER CHAIN TRANSFER  
CONSTANTS FOR METHYL ACRYLATE AND ETHANETHIOL AT 50°

Run no.	Mole ratio EtSH-acrylate	Mole % AIBN (compared to EtSH)	Time, hr.	Methyl acrylate consumed, %	Mole ratio, one-unit-two-unit	Mole ratio, two-unit-three-unit
1	0.202	0.28	3.2	5.4	0.590	
2	.457	.26	2.0	7.4	.801	
3	.712	.25	1.1	3.3	.969	
4	.854	.28	1.0	5.0	1.100	
5	.960	.21	1.0	10.0	1.182	
6	1.220	.27	0.6	9.4	1.385	
7	0.130	.38	4.5	4.7		0.550
8	.189	.34	2.7	5.1		.715
9	.444	.25	1.4	2.8		.995
10	.655	.22	1.5	8.6		1.270
11	.842	.12	1.0	9.8		1.810

Determination of the polymerization chain transfer constant  $C_\infty$  was complicated by the fact that methyl acrylate interferes seriously with the amperometric titration method of Kolthoff and Harris<sup>6</sup> under the usual conditions presumably because of the rapid base-catalyzed addition of mercaptan to acrylate on mixing with ammonia. It was found, however, that in mixtures containing enough mercaptan to titrate with small aliquots, results within 2% of the values found in the absence of acrylate could be obtained consistently by

(6) I. M. Kolthoff and W. E. Harris, *Ind. Eng. Chem., Anal. Ed.*, **18**, 161 (1946).

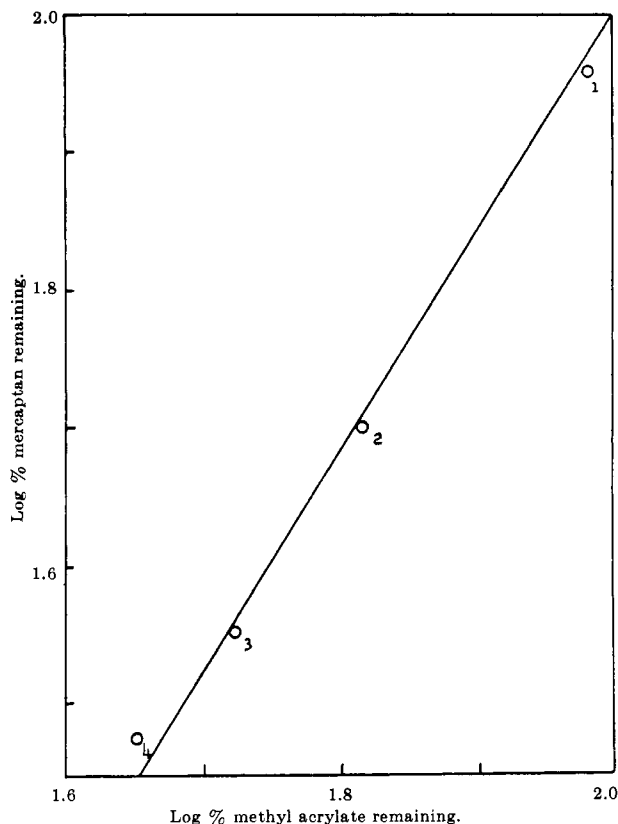


Fig. 2.—Data for determination of polymerization chain transfer constant.

rapid titration below 10° using reduced base concentration (see Experimental). Data for this are recorded in Table III and plotted in Fig. 2.

TABLE III  
DATA FOR CALCULATION OF  $C_{\infty}$  FOR METHYL ACRYLATE AND ETHANETHIOL AT 50°

Run no. <sup>a</sup>	Methyl acrylate remaining, %	Log % methyl acrylate remaining	Ethanethiol remaining, %	Log % ethanethiol remaining
1	97.0	1.986	91.0	1.959
2	65.9	1.819	50.2	1.702
3	53.2	1.726	35.7	1.553
4	45.0	1.654	30.4	1.477

<sup>a</sup> Mixtures contained 0.0145 mole of thiol per mole of monomer.

Values of the chain transfer constants together with statistical estimates of their reproducibility are summarized in Table IV.

### Discussion

The value reported here for  $C_{\infty}$  agrees well with the value of 1.69 reported by Walling<sup>7</sup> for methyl acrylate and butanethiol on the basis of measurements using radioactive sulfur. The value for  $C_1$  appears to be smaller by the same order of magnitude as in the case of styrene and ethanethiol.

The values for  $C_2$  are consistent with each other. They are also remarkably close to  $C_{\infty}$  and suggest that

(7) C. Walling, *J. Am. Chem. Soc.*, **70**, 2561 (1948).

TABLE IV  
SUMMARY OF CHAIN TRANSFER CONSTANT DATA ON METHYL ACRYLATE AND ETHANETHIOL AT 50°

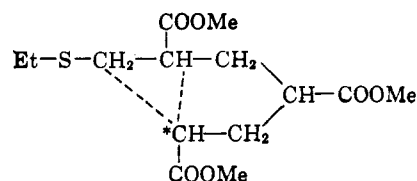
Constant	Fig.	Table	Value <sup>a</sup>	Standard deviation	Estimated error <sup>b</sup>
$C_1$	1	II	0.78	0.0111	$\pm 0.03$
		II	0.434	0.0109	$\pm .030$
$C_2$	1	II	1.79		$\pm .15^c$
		II	1.61	0.111	$\pm .35$
$C_2$	1	II	0.33	0.082	$\pm .26$
		II	5		$-2.0 + 19^c$
$C_{\infty}^d$	2	III	1.57	0.043	$\pm 0.18$

<sup>a</sup> Values are based on least squares calculation assuming linearity. <sup>b</sup> 5% probability level. <sup>c</sup> Based on intercept limits. <sup>d</sup> One fixed point assumed with 100% of both reactants remaining.

the two-unit radical is not appreciably less active than the polymer radical in spite of the fact that the active end should be most favorably placed to interact directly with the sulfur.

The high value for  $C_3$  strongly suggests a reactivity minimum for the three-unit radical similar to that reported for the styrene bromotrchloromethane system.<sup>3b</sup> Unfortunately, the data does not give so reliable a value for  $C_3$  as for  $C_2$ , and some apparent increase may arise from the small decrease in the monomer to thiol ratio during the reaction. This means that points should be plotted a little further to the left in Fig. 1 raising the intercept slightly. However, a value of  $C_3$  as low as  $C_2$  and  $C_{\infty}$  would require an intercept of unity, which seems to be exceedingly improbable.

In considering possible explanations, it should be pointed out that the reactive end of the three-unit radical appears favorably placed to abstract a hydrogen



reversibly from either the first or second carbon atom along the chain from the sulfur. In either case a more stable radical having less relative tendency to propagate might result. It seems conceivable that the proximity of sulfur or other polarizable end-group atoms having available orbitals might facilitate such exchanges. Since our data gives no information on  $C_4$ , it is possible that the chain transfer constant maximum and the reactivity minimum may be further down the chain (*cf.* ref. 3a and 3d). Such a finding would be harder to explain. There is need for more data on relative and absolute rates of formation of individual telomers as well as termination rates for individual radicals of known length. Such studies are planned in this laboratory.

The two- and three-unit telomers have potential interest as synthetic intermediates (*cf.* cyclic compounds from similar products<sup>8</sup>). We currently are studying cotelomers formed from acrylate esters with styrene and other monomers to extend these possibilities.

(8) G. Schreyer and T. Voelker, *Makromol. Chem.*, **68**, (1963).