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The Telomerization of Methyl Acetate and Methyl Cyanoacetate with Ethylene

Tsutomu FUJIMOTO and Ichiro HIRAO

Laboratory of Organic Synthesis, Department of Chemical Engineering, Kyushu Institute of Technology, Tobata-ku, Kita-kyushu 804

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The telomerization of methyl acetate and cyanoacetate with ethylene initiated by di-*tert*-butyl peroxide was investigated. Methyl esters of linear and α-branched alkanoic acids, and linear and α-branched alkyl acetates, as well as hydrocarbons, were identified in the system of methyl acetate. The methyl esters of linear and α-branched α-cyanoalkanoic acids were identified in the system of methyl cyanoacetate, but no alkyl cyanoacetates could be found. It was suggested that intramolecular 1,5-hydrogen transfer in telomer radicals with two ethylene units and a chain-transfer reaction to the telomers gave the branched telomers. The chain-transfer constants were estimated in the system of methyl cyanoacetate. The introduction of the cyano group to methyl acetate at the α-position gave a favorable system for chain-transfer reactions and facilitated intramolecular 1,5-hydrogen transfer in the telomer radicals. The relatively higher relative reactivity of the methoxy group to the acetyl group in methyl acetate in the telomerization with ethylene was discussed.

It is well known that a homolytic abstraction of an α-hydrogen atom from acetic and α-substituted acetic acids and their esters preferentially give the carboxymethyl radical and its homologous radicals.[1–3] The radicals react with olefins to give telomeric products.[4] The telomerization of ethylene with acetic acid and its derivatives is accompanied by 1,5-hydrogen transfer in telomer radicals, α-branched telomers being formed together with linear telomers.[5–7] Propagation, chain-transfer, and intramolecular hydrogen-transfer reactions of methoxycarbonylalkyl and cyanomethoxycarbonylalkyl radicals may be expected in the telomerization of methyl acetate and cyanoacetate with ethylene. An elucidation of the behavior of these radicals will give information of interest with regard to the reactivity of substituted alkyl radicals.

Some homologous series of telomers may be expected in the telomerization of methyl acetate with ethylene, but only linear aliphatic acids have been isolated from the telomerization products.[8] Free radical additions of ethyl cyanoacetate to unsaturated compounds have also been investigated,[9–14] but there has been no report on the telomerization of methyl cyanoacetate with ethylene. This paper will describe the telomerization products and the chain-transfer and intramolecular-rearrangement reactions of the telomer radicals in the telomerization of methyl acetate and cyanoacetate with ethylene.

Results and Discussion

Telomerization Products of Methyl Acetate with Ethylene. The telomerization was carried out in the presence of radical initiators in an autoclave. The product of the telomerization was fractionated into three fractions: I (insoluble in hot methyl acetate), II (soluble in hot methyl acetate, but insoluble at room temperature), and III (soluble in methyl acetate at room temperature). A product with a high molecular weight was obtained under an initial ethylene pressure of 40 kg/cm^2, but a product with a mean molecular weight of 235 was obtained using di-*tert*-butyl peroxide (DTBP) when ethylene was introduced to keep a pressure of 20 kg/cm^2 at 140 °C during the reaction. The product thus obtained was further fractionated to three fractions, III-1 (bp 60—150 °C/60 mmHg), III-2 (bp 150/60—170 °C/5 mmHg), and the residue (III-3). The compositions and molecular weights of the fractions are given in Table 1.

TABLE 1. COMPOSITION AND MOLECULAR WEIGHT OF THE FRACTIONS OF METHYL ACETATE TELOMER

Initiator	AIBN	DTBP	DTBP
Initial ethylene Press. (kg/cm^2)	40	40	20[a]
Temp. (°C)	80	130	140
Time (hr)	7	7	8
Yield (g)	11.8	49.2	29.8
Composition (wt%) and M.wt.[b]			
I	73.3 (2400)	71.4 (1550)	—
II	16.1 (595)	22.3 (545)	—
III	10.6 (350)	6.3 (280)	100 (235)
III-1	—	—	37.5 (139)
III-2	—	—	39.7 (240)
III-3	—	—	22.8 (384)

a) Pressure of 20 kg/cm^2 was kept at 140 °C. b) Molecular weights are given in parentheses.

The gas chromatogram of lower boiling products is shown in Fig. 1. The identification of the products was carried out by gas chromatography (glc) and by a study of the IR, NMR, and mass spectra (see Experimental). The a_n peaks (n=1—7) were identified with methyl butanoate (LA_1), hexanoate (LA_2), octanoate (LA_3), decanoate (LA_4), dodecanoate (LA_5), tetradecanoate (LA_6), and hexadecanoate (LA_7) respectively. The b_n peaks (n=1—7) were identified with propyl (LM_1), pentyl (LM_2), heptyl (LM_3), nonyl (LM_4), undecyl (LM_5), tridecyl (LM_6), and pentadecyl (LM_7) acetates respectively. The c_n peaks (n=1—5) were identified with methyl 2-ethylbutanoate (BA_1), 2-ethylhexanoate (BA_2), 2-butylhexanoate (BA_3), 2-ethyloctanoate (BA_4), and 2-butyloctanoate (BA_5) respectively. The d_n peaks (n=1—3) were identified with

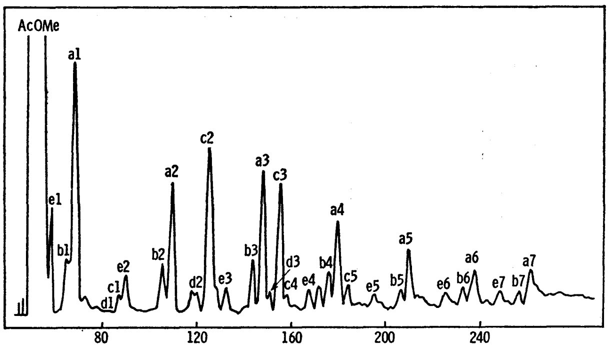

Fig. 1. Gas chromatogram of the telomerization product of methyl acetate with ethylene.

1-ethylpropyl (BM_1), 1-ethylpentyl (BM_2), and 1-butylpentyl(BM_3) acetates respectively. Although a peak which corresponds to 1-butylheptyl acetate in the retention time could not be detected because of the overlap of other peaks, the presence of the acetate was suggested by the formation of undecan-5-ol after the saponification of the telomerization product. The e_n peaks (n=1—7) were hydrocarbon homologues with an odd number of carbon atoms, from nonane to heneicosane respectively. The hydrocarbons were presumably formed by the addition of methyl radicals to ethylene. The result of silica-gel-column chromatography showed that hydrocarbons were included (at least 12% by weight) in the product obtained under a pressure of 20 kg/cm^2 at 140 °C. Chiang and Li have isolated and identified only linear acids from the same telomerization,[8] but the telomerization product was a complex mixture containing methyl esters of α-branched alkanoic acids (BA), linear alkyl (LM), and α-branched alkyl (BM) acetates and hydrocarbons in addition to methyl esters of linear alkanoic acids (LA).

The amounts of telomers relative to the amount of BA_2 were determined by glc because no suitable internal standard could be found. The results are given in Table 2. The content of the LA_1 telomer was 42% at 160 °C, while the contents of LA, BA, LM, and BM were 46—57, 24—29, 18—21, and 2—5% respectively in the telomers detectable by glc (Table 3).

Table 2. Relative amounts of methyl acetate telomers[a)]

Temp. (°C)	140	140	140	140	140	130	150	160
Press. (kg/cm^2)	20	20	20	30	40	20	20	20
Time (hr)	1	3	8	5	5	3	2	1
LA_1	1.91	1.92	1.91	1.72	1.53	0.99	2.45	2.68
LA_2	0.80	0.81	0.82	0.94	1.05	0.68	0.69	0.61
LA_3	0.63	0.62	0.61	0.94	1.20	0.82	0.41	0.23
LA_4	0.33	0.30	0.33	0.55	0.92	0.41	0.14	0.07
LA_5	0.18	0.13	0.16	0.36	0.68	0.28	0.06	—
LA_6	0.15	0.11	0.13	0.30	0.58	0.28	—	—
LM_1	0.42	0.44	0.44	0.37	0.30	0.20	0.49	0.52
LM_2	0.34	0.34	0.34	0.31	0.32	0.31	0.35	0.38
LM_3	0.25	0.26	0.24	0.26	0.30	0.25	0.21	0.15
LM_4	0.22	0.19	0.19	0.25	0.30	0.23	0.13	0.07
LM_5	0.14	0.11	0.13	0.21	0.28	0.19	0.06	—
LM_6	0.12	0.10	0.11	0.19	0.28	0.18	—	—
LM_7	0.09	0.09	0.09	0.17	0.24	0.20	—	—
BA_1	0.13	0.18	0.20	0.15	0.14	0.13	0.20	0.23
BA_2	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
BA_3	0.67	0.62	0.63	0.84	1.05	0.81	0.29	0.14
BA_4	0.07	0.11	0.11	0.13	0.12	0.07	0.08	0.06
BA_5	0.15	0.13	0.14	0.23	0.31	0.19	0.07	0.06
BM_1	0.03	0.04	0.05	0.05	0.04	0.01	0.02	0.02
BM_2	0.12	0.15	0.19	0.16	0.19	0.14	0.10	0.07
BM_3	0.11	0.13	0.13	0.13	0.16	0.12	0.07	0.05

a) Relative amounts of telomers are represented in mol/mol of methyl 2-ethylhexanoate (BA_2).

Table 3. Composition of series of methyl acetate telomers

Temp. (°C)	140	140	140	140	140	130	150	160
Press. (kg/cm^2)	20	20	20	30	40	20	20	20
Time (hr)	1	3	8	5	5	3	2	1
LA_1 (%)	24	25	24	19	14	13	36	42
LA (%)	51	50	50	52	54	46	55	57
LM (%)	20	20	19	19	18	21	18	18
BA (%)	26	26	26	26	24	29	24	24
BM (%)	3	4	5	4	4	4	3	2

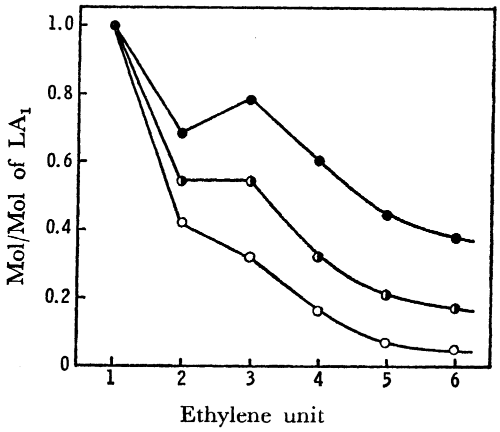

Fig. 2. Effect of ethylene pressure on the distribution of series LA at 140 °C.
Pressure
-○-: 20 kg/cm², -◑-: 30 kg/cm², -●-: 40 kg/cm².

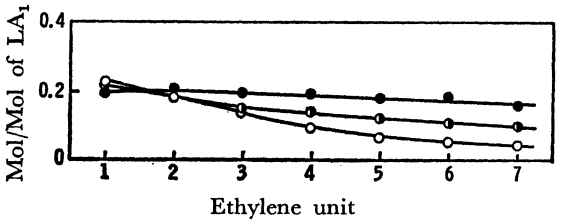

Fig. 3. Effect of ethylene pressure on the distribution of series LM at 140 °C.
Pressure
-○-: 20 kg/cm², -◑-: 30 kg/cm², -●-: 40 kg/cm².

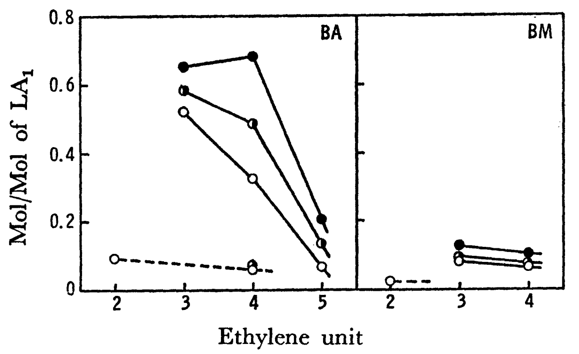

Fig. 4. Effect of ethylene pressure on the distribution of series BA and BM at 140 °C.
Pressure
-○-: 20 kg/cm², -◑-: 30 kg/cm², -●-: 40 kg/cm².
Full lines indicate butyl branched telomers.

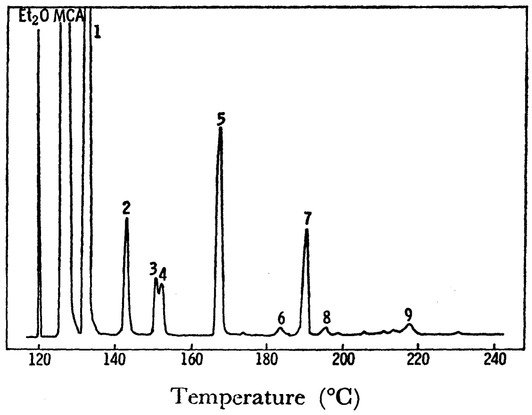

Fig. 5. Gas chromatogram of the telomerization product of methyl cyanoacetate with ethylene.

The distributions of the telomers were almost unaffected by the reaction time. The effects of the pressure of ethylene on the distributions of LA, LM, BA, and BM are shown in Figs. 2, 3, and 4. In the distribution of LA, a remarkable minimum was found at two ethylene units, while a maximum at four ethylene units in the distribution of the methyl ester telomers with a branch of the butyl group under a high pressure of ethylene.

Telomerization Products of Methyl Cyanoacetate with Ethylene. The telomerization was carried out in the presence of DTBP at 140 °C in an autoclave. Ethylene was introduced into the autoclave to keep the prescribed pressure during the reaction. The gas chromatogram of the reaction mixture is shown in Fig. 5. The reaction products were identified by glc and by mass spectrometry (see Experimental). The 1, 4, and 6 peaks were identified with methyl 2-cyanobutanoate (N_1), 2-cyanohexanoate (N_2), and 2-cyanooctanoate (N_3) respectively. The 2, 5, 7, 8, and 9 peaks were identified with methyl 2-cyano-2-ethylbutanoate (B_1), 2-cyano-2-ethylhexanoate (B_2), 2-butyl-2-cyanohexanoate (B_3), 2-cyano-2-ethyloctanoate (B_4), and 2-butyl-2-cyanooctanoate (B_5) respectively. No propyl and pentyl cyanoacetates, which were expected to be formed *via* cyanoacetoxymethyl radicals, could be detected by glc. The component of the 3 peak was confirmed to be methyl 2-cyano-3-methyl-2-butenoate, which was a product of the thermal decomposition of DTBP in methyl cyanoacetate without ethylene, by a study of the IR, NMR, and mass spectra. A small amount of higher-boiling materials (bp$>$110 °C/1 mmHg) was also obtained; however, the IR and NMR spectra showed the presence in the fraction of a few telomers with higher ethylene units.

The analysis of the telomerization products was carried out by means of glc. The results are given in Table 4. The content of the N_1 telomer was over 50%, and a remarkable formation of the branched telomers, especially B_2, was observed in this system.

Chain-transfer Reactions in Telomerization of Methyl Cyanoacetate with Ethylene. In the telomerization, linear telomers, N_n, may be formed by the chain-transfer reaction of linear telomer radicals formed from cyanomethoxycarbonylmethyl radicals. The branched telomer, B_1, may be formed *via* the addition of ethylene to 1-cyano-1-methoxycarbonylpropyl radicals. The increase in the amount of B_1 with the reaction time suggests that the radicals were produced by the abstraction of a hydrogen atom at the α-position in the linear telomer N_1. The formation of the radicals by 1,3-hydrogen transfer in 3-cyano-3-methoxycarbonylpropyl radicals is presumed to be negligible because of the small possibility of 1,3-hydrogen transfer.15) The formation of B_1, therefore, suggests that a part of the branched telomers may be formed by chain transfer to linear

Table 4. Composition of methyl cyanoacetate telomers[a)]

Press. (kg/cm^2) Time (hr)	20 8	30 1	30 3	30 8	40 8
N_1	175 (63.6)	121 (62.3)	158 (56.5)	165 (54.5)	160 (49.4)
N_2	12.1 (4.4)	9.4 (4.8)	13.9 (5.0)	14.6 (4.8)	17.7 (5.5)
N_3	0.6 (0.2)	0.7 (0.4)	1.0 (0.4)	1.1 (0.4)	1.9 (0.6)
$HE_{\geq 4}CH$[b)]	0.0 (0.0)	0.1 (0.0)	0.1 (0.0)	0.2 (0.1)	0.3 (0.1)
B_1	30.9 (11.2)	11.6 (6.0)	25.0 (8.9)	31.0 (10.2)	26.2 (8.1)
B_2	46.9 (17.0)	38.4 (19.8)	61.1 (21.8)	69.0 (22.8)	81.7 (25.2)
B_3	8.8 (3.2)	11.2 (5.8)	17.7 (6.3)	19.0 (6.3)	30.2 (9.3)
B_5	0.5 (0.2)	1.1 (0.6)	1.7 (0.6)	1.7 (0.6)	3.8 (1.2)
$HE_1CE_{\geq 3}H$[b)]	0.5 (0.2)	0.5 (0.3)	1.1 (0.4)	1.3 (0.4)	2.0 (0.6)
$HE_2CE_{\geq 4}H$[b)]	0.0 (0.0)	0.1 (0.0)	0.1 (0.0)	0.1 (0.0)	0.4 (0.1)
$[C_2H_4]/[MCA]$[c)]	0.028	0.040	0.042	0.042	0.058
$[C_2H_4]$[d)]	0.27	0.42	0.42	0.42	0.57

a) Yield and composition in parentheses are given in mmol and mol%, respectively. b) C and E in the telomer symbol represent $\rangle C(CN)COOCH_3$ and ethylene unit, respectively. Yield was estimated. c) The average ratio of ethylene and methyl cyanoacetate concentrations during the reaction. d) The average concentration of ethylene during the reaction.

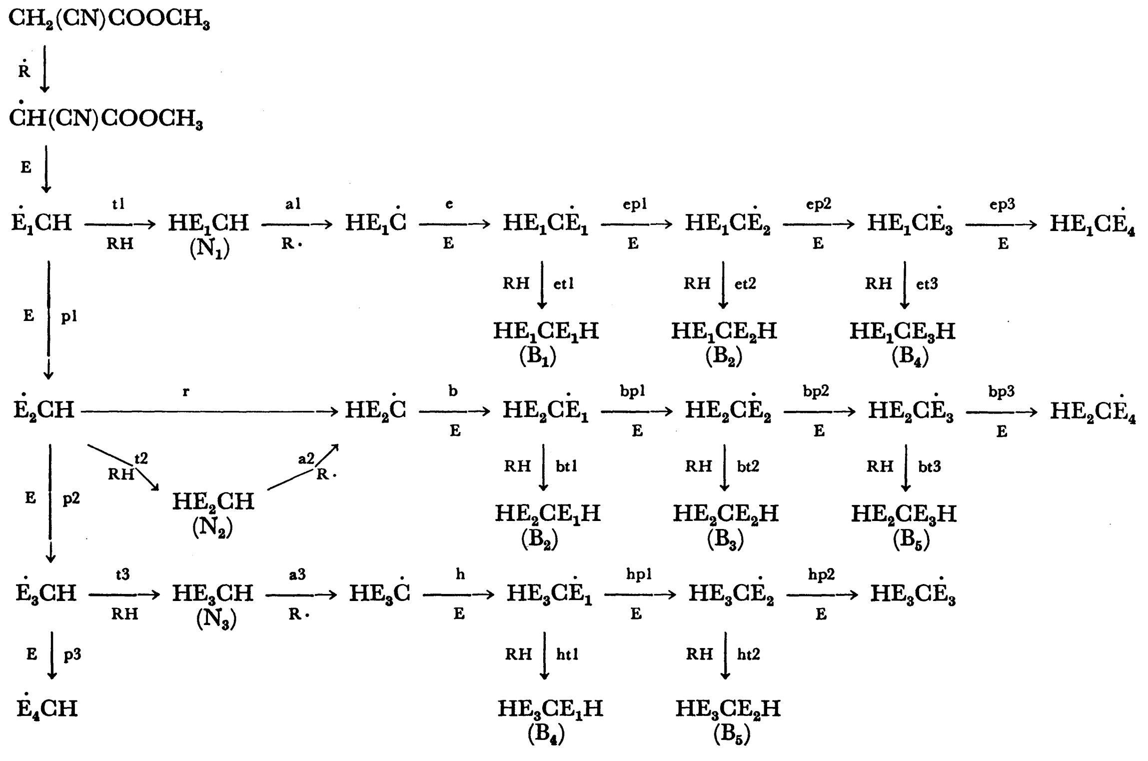

Chart 1. Reaction of methyl cyanoacetate with ethylene. C and E in the telomer symbol HE_nCE_mH represent $\rangle C(CN)COOCH_3$ and ethylene unit, respectively. RH, E and R· represent chain transfer agent, ethylene and a free radical, respectively.

telomers.

The B_2 telomer may be formed by Reaction et2 from 5-cyano-5-methoxycarbonylheptyl radicals and by Reaction bt1 from 3-cyano-3-methoxycarbonylheptyl radicals (Chart 1). A part of the latter radicals may be formed through chain-transfer reaction to N_2 (a2); however, most of the radicals may be formed *via* intramolecular 1,5-hydrogen transfer in 5-cyano-5-methoxycarbonylpentyl radicals, which are telomer radicals with two ethylene units. The intramolecular 1,5-hydrogen transfer was suggested by the remarkable formation of the B_2 telomer, even at an initial stage of the reaction. Intramolecular 1,5-hydrogen transfer reaction is known in alkyl radicals in the gas phase[15] and has been suggested in the telomerization of ethylene with acetic acid and its derivatives.[5-7] Therefore, most of the telomers with a branch of the butyl group at the α-position may be formed from the radicals produced by the intramolecular hydrogen transfer. The possible formation pathways of the telomers identified in the system are summarized in Chart 1.

An estimation of the conversions (A_n and R) of the linear telomer N_n to branched telomers *via* chain-transfer to the telomer and of 5-cyano-5-methoxycarbonylpentyl radicals to branched telomers *via* intramolecular 1,5-hydrogen transfer in the radicals was attempted on the basis of the yields of telomers. For the estimation, it was necessary to determine the yields of branched telomers in each pathway. The yields were estimated from the following relations by assuming the same chain-transfer constant for the telomer radical, $RC(CN)(COOCH_3)\dot{E}_n$ (R=Et, Bu, and hexyl; E represents an ethylene unit), with the same n;

$$\frac{[B_2]_{et2}}{[B_1]_{et1}} = \frac{[B_3]_{bt2}}{[B_2]_{bt1}} = \frac{[B_5]_{ht2}}{[B_4]_{ht1}}$$

$$\frac{[B_4]_{et3}}{[B_2]_{et2}} = \frac{[B_5]_{bt3}}{[B_3]_{bt2}}$$

where $[B_n]_{etn}$, $[B_n]_{btn}$, and $[B_n]_{htn}$ represent the yields of branched telomers formed in the et*n*, bt*n*, and ht*n* pathways respectively. There is no information on the chain-transfer constants of the branched telomer radicals; however, we may expect little change in the constants caused by the difference in alkyl groups, such as ethyl, butyl, and hexyl, in the telomer radical. A slight change may also be expected from the ratios (1.0—1.5)[6,7] of the chain-transfer constant of the branched telomer radical $BuC(X)(COOCH_3)\dot{E}_n$ to that of the linear telomer radical $CH(X)(COOCH_3)\dot{E}_n$ in the telomerizations of methyl propionate ($X=CH_3$) and methyl chloroacetate (X=Cl) with ethylene. The results, and the estimated conversions of linear telomer radicals with ethylene units of n by Reaction t*n* (T_n) and of branched telomer radicals $HE_2C(CN)(COOCH_3)\dot{E}_n$ by Reaction bt*n* (T_{bn}), are given in Table 5. The mean value of A_1 and A_3 was used for A_2 in the estimation of the conversion, R. It was found that 5-cyano-5-methoxycarbonylpentyl radicals gave branched telomers in conversions of 75—79% under the present conditions.

Table 5. Conversion of telomer radicals

Press. (kg/cm²) Time (hr)	20 8	30 1	30 3	30 8	40 8
T_1[a]	77.4	70.4	68.7	68.3	61.1
T_2	23.7	19.0	21.4	21.4	19.3
R	75.1	79.2	76.7	76.6	78.1
T_{b1}	81.2	73.7	73.1	74.1	67.4
T_{b2}	94.9	90.6	91.3	92.1	88.6
A_1	17.9	11.5	17.8	20.2	19.5
A_3	18	17	34	37	34

a) Conversions are given in percentage.

The chain-transfer constants, C_n (k_{tn}/k_{pn}), for a linear telomer radical, $\dot{E}_nCH(CN)COOCH_3$, and C_{bn} (k_{btn}/k_{bpn}) for a branched telomer radical, $HE_2C(CN)(COOCH_3)\dot{E}_n$, were estimated by Mayo's equation[16] from the estimated yields of the telomers and from the average ratio of the ethylene and methyl cyanoacetate concentrations. The C_{rp} ratio of the rate constants, k_r (Reaction r) to k_{p2} (Reaction p2), was evaluated from the estimated yields of the branched telomers formed *via* Reaction r ($[B_n]_r$) and those of all of the linear and branched telomers formed *via* Reaction p2 ($[N_n+B_n]_{p2}$), and from the average concentration of ethylene;[7]

$$C_{rp} = \frac{k_r}{k_{p2}} = \frac{[B_n]_r[E]}{[N_n+B_n]_{p2}}$$

The estimated chain-transfer constants and C_{rp} values are given in Table 6. In the estimation, the formation of N_2 from 1-cyano-1-methoxycarbonylpentyl radicals by hydrogen abstraction was neglected.[6,7] Although the chain-transfer constant of the radical cannot be estimated, it should be much smaller than C_1 for the radicals stabilized by cyano and methoxycarbonyl groups. If the constant is not negligible, some higher value may be estimated for C_{rp} and some lower value for C_2. The estimated chain-transfer contants and C_{rp} values were larger than those in the telomerization

Table 6. Chain transfer constants

Press. (kg/cm²) Time (hr)	20 8	30 1	30 3	30 8	40 8	(Mean)
C_1	0.096	0.095	0.092	0.090	0.092	0.093
C_2	0.57	0.42	0.49	0.44	0.44	0.47
C_{b1}	0.12	0.11	0.11	0.12	0.12	0.12
C_{b2}	0.52	0.39	0.44	0.49	0.45	0.46
C_{rp}[a]	32	43	36	36	40	37

a) Represented in mol/l.

of methyl propionate and methyl chloroacetate with ethylene.[6,7]

Chain-transfer Reactions in the Telomerization of Methyl Acetate with Ethylene. In the telomerization product, telomers of methyl esters and acetates were found. The formation of these telomers suggests that hydrogen atoms of acetyl and methoxy groups in methyl acetate were abstracted to give methoxycarbonylmethyl and acetoxymethyl radicals. The formation of branched methyl ester telomers BA by chain transfer to linear telomers LA was also suggested by the formation of the BA_1 branched telomer. Intramolecular 1,5-hydrogen transfer in 5-methoxycarbonylpentyl radicals was also suggested by the minimum in the distribution of the LA telomer at two ethylene units (Fig. 2) and by the remarkable formations of BA_2 and of branched methyl ester telomers with a butyl group at the α-position. The formation of branched acetate telomers may be similar to that of methyl ester telomers, BA, as the formation of BM_1 and the amount of BM_2 suggest. These pathways of the formation of branched telomers are the same in manner as those in the system of methyl cyanoacetate.

The degree of chain transfer to linear telomers, LA, cannot be estimated because not all of the telomers could be analyzed by glc, but a convresion of more than 9% of the LA_1 formed during the reaction to the branched telomers was evaluated from the ratio of the amount of BA_1 to the sum of the amounts of LA_1 and BA_1 for 8 hr under a pressure of 20 kg/cm^2 at 140 °C. A considerable extent of the intramolecular hydrogen transfer in 5-methoxycarbonylpentyl radicals was also suggested by the ratio (1.6) of the sum of the amounts of BA_2, BA_3, and BA_5 to that of LA_3, LA_4, and LA_5, although it means only a rough measure.

A significant degree of the formation of branched telomers was also shown by the compositions of the series of telomers in the entire product (Table 7).

Table 7. Relative ratio of series of the telomers

Temp. (°C)	20	130	140	150	160
LA	—	1.00	1.00	1.00	1.00
LM	—	0.41	0.37	0.36	0.33
BA	—	0.74	0.61	0.47	0.32
BM	—	0.12	0.10	0.04	0.02
BA/LA	—	0.74	0.61	0.47	0.32
BM/LM	—	0.29	0.27	0.11	0.06
$(M/A)_t$	—	0.30	0.29	0.27	0.26
$(M/A)_d$	1.47	0.93	0.83	0.80	—
$(M/A)_0$	1.15	—	0.26	—	—

The compositions were obtained by means of NMR as follows:

$$LA = H_d - H_e/3$$

$$LM = H_f/2$$

$$BA = 2H_e/3 - H_d$$

$$BM = H_c/3 - H_f/2$$

where H_c, H_e, H_f, and H_d represent the relative intensities of the protons of CH_3COO-, $-COOCH_3$, $-COOCH_2-$, and of the sum of the protons of $-CH_2COO-$ and $>CHCOO-$ respectively. The high ratio of the branched telomer, BA, to the linear telomer, LA, was observed under a pressure of 20 kg/cm^2 at 130—140 °C, and the ratio decreased with a rise in the reaction temperature. In acetate telomers, the ratio (BM/LM) of branched to linear telomers also shows a tendency similar to that of methyl ester telomers. However, the lower ratio of BM/LM suggests that the α-hydrogen of the alkoxy moiety in the acetates is less reactive as a whole for homolytic hydrogen abstraction than that of the carboxylic moiety in the methyl esters.

The chain-transfer constants of the telomer radicals in this system could not be evaluated, but the broad distributions of the LA and LM telomers suggest quite small-chain-transfer constants of ω-methoxycarbonylalkyl and ω-acetoxyalkyl radicals (Figs. 2 and 3). A lower reactivity of ω-acetoxyalkyl radicals in the chain-transfer reaction than that of the ω-methoxycarbonylalkyl radicals was also suggested by the broader distribution in the acetate telomers, LM. The sharp distribution of the cyanoacetate telomers, N_n, compared with that of the methyl ester telomers, LA, shows that the introduction of the cyano group to methyl acetate at the α-position gave a favorable system for a chain-transfer reaction.

Relative Reactivity of the Methoxy Group to the Acetyl Group. In the telomerization of methyl acetate with ethylene, the abstraction of a hydrogen atom from methoxy and acetyl moieties in methyl acetate was indicated by the formation of acetate and methyl ester telomers. The relative reactivity of the methoxy group to the acetyl group in methyl acetate for hydrogen abstraction was estimated by means of the ratio ($(M/A)_t$) of the amounts of acetate telomers to that of methyl ester telomers in the telomerization. The ratio was 0.30 at 130 °C; it was slightly decreased with a rise in the reaction temperature (Table 7). The ratio suggests that the relative reactivity of the methoxy group is higher than that of the alkoxy moiety to the acetyl group in ethyl and isopropyl acetates.[17] Therefore, it was compared with the ratio ($(M/A)_d$) of the amount of the acetoxy group to that of the methoxycarbonyl group in the product of the decomposition of DTBP in methyl acetate, and with the formation ratio ($(M/A)_0$) of nonyl acetate to methyl decanoate in the addition of methyl acetate to 1-octene initiated by DTBP. The $(M/A)_d$ ratio was estimated from the ratio of the proton intensity of the acetyl group to that of the methoxy group in the product, which contained mainly methyl succinate, ethylene diacetate, and methyl 3-acetoxypropionate. The $(M/A)_0$ ratio was measured by means of glc. The ratios of $(M/A)_d$ and $(M/A)_0$ are given in Table 7.

The $(M/A)_d$ and $(M/A)_0$ ratios suggest that the methoxy group is more reactive for hydrogen abstraction than the acetyl group at 20 °C, and that the relative reactivity of the methoxy group decreases with a rise in the temperature. The value of $(M/A)_0$ was the same as that of $(M/A)_t$ at 140 °C; it was presumed to be higher than that in the addition of 1-octene with methyl acetate initiated by di-isopropyl peroxydicarbonate.[18]. The $(\mathrm{M/A})_d$ ratio at the same temperature showed that the relative reactivity of the methoxy group was higher in the absence of ethylene or 1-octene. The difference in the relative reactivity of the methoxy group may be caused by a difference in the extent of contributions of the *tert*-butoxy, methyl, and telomer radicals to hydrogen abstraction from methyl acetate. In the decomposition of DTBP in methyl acetate, a hydrogen atom of methyl acetate may be abstracted by the methyl and *tert*-butoxy radicals formed by the decomposition of DTBP. Methyl radicals predominantly abstract a hydrogen atom from the acetyl group in methyl acetate,[19] whereas a hydrogen atom of the methoxy group in methyl acetate may be abstracted mainly by electrophilic *tert*-butoxy radicals.[20] Therefore, the high value of $(\mathrm{M/A})_d$ may be attributed to the large extent of the contribution of *tert*-butoxy radicals to the hydrogen abstraction. In the presence of olefins, the relative reactivity of the methoxy group may be apparently decreased by the contribution of additional hydrogen abstraction by telomer radicals, which are expected to be similar reactive with alkyl radicals in hydrogen abstraction. The relatively higher values of $(\mathrm{M/A})_t$ and $(\mathrm{M/A})_0$ may be caused by some contribution of *tert*-butoxy radicals to the hydrogen abstraction in the telomerizations with short kinetic chain lengths.

Experimental

Materials. Commercial methyl acetate was treated with acetic anhydride and with potassium carbonate in the usual way, then distilled. Commercial methyl cyanoacetate was dried over anhydrous magnesium sulfate, then distilled. Commercial 1-octene was distilled. The DTBP, ethylene, and methyl esters of linear alkanoic acids were obtained commercially. The methyl esters of α-branched alkanoic acids were prepared from the corresponding acids and methanol. The methyl 2-cyanoalkanoates and 2-alkyl-2-cyanoalkanoates were prepared from alkyl bromides and methyl cyanoacetate or the corresponding methyl 2-cyanoalkanoates.[21] Acetates and cyanoacetates were prepared from the corresponding alcohols and acetyl chloride or cyanoacetic acid. These reference samples were confirmed by elemental analyses and by a study of the IR and NMR spectra.

Telomerization. *Procedure A*: A mixture of methyl acetate (100 g) and an initiator (0.015 mol/mol) was placed in a 300 ml stainless-steel autoclave, air was displaced with ethylene, and ethylene was introduced until a pressure of 40 kg/cm^2 was reached at room temperature. The mixture was then heated at the prescribed temperature with stirring. *Procedure B*: A mixture of 150 g of methyl acetate and 7.5 g of DTBP was heated at the prescribed temperature in the autoclave. During the reaction, ethylene was introduced to keep the pressure prescribed for that temperature.

The telomerization of methyl cyanoacetate with ethylene was carried out by Procedure B, using 150 g of methyl cyanoacetate and 4.4 g of DTBP.

Hydrolysis of Telomers. A mixture of 7.6 g of the telomerization product of methyl acetate with ethylene, 5.0 g of potassium hydroxide, and 50 ml of ethanol was heated at 180 °C for 8 hr in an autoclave. The aicd (5.0 g) and the neutral fractions (1.9 g) were subsequently separated in the usual way.

Separation of Hydrocarbons. Hydrocarbons (0.127 g) were separated from the telomerization product (1.014 g) of methyl acetate with ethylene using a silica-gel-column with petroleum ether.

Identification of the Products. A gas chromatographic determination was made on 2.25 m and 4.0 m columns packed with PEG-20M (30% on Celite 545) for the telomerization products of methyl acetate with ethylene, and on a 2.25 m column packed with Apiezone Grease L (30% on Celite 545) for the telomerization products of methyl cyanoacetate with ethylene, with helium as the carrier gas. The IR and NMR spectra were measured on JASCO IR-A2 and JEOL JNM-C-60HL spectrometers respectively. The mass spectra were measured on a Hitachi RMU-6L mass spectrometer combined with a gas chromatograph. The reaction mixture was fractionated by the use of a spinning-band column.

Methyl Alkanoates LA$_n$: The retention times (min) of LA$_1$—LA$_4$, measured using a 4.0 m column at 140 °C and of LA$_5$—LA$_7$, measured using a 2.25 m column at 240 °C, agreed with those of authentic methyl esters as follows (LA$_n$, the retention time, reffered to methyl ester, and its retention time): LA$_1$, 1.75, butanoate, 1.72; LA$_2$, 4.45, hexanoate, 4.40; LA$_3$, 11.10, octanoate, 11.06; LA$_4$, 27.76, decanoate, 27.75; LA$_5$, 3.01, dodecanoate, 2.99; LA$_6$, 5.21, tetradecanoate, 5.22; LA$_7$, 9.02, hexadecanoate, 8.97. The IR and NMR spectra of LA$_n$ (n=1—5), which were collected by preparative glc, and the mass spectra of LA$_n$(n=1−7) also supported the above identification. The signals in the NMR spectra were as follows (signal, τ value, and assignment): a, 9.07—9.15(t), $\mathrm{CH_3}$–; b, 8.35—8.77 (m), –$\mathrm{CH_2}$–; c, 7.82−7.84 (t), –$\mathrm{CH_2COO}$–; d, 6.48—6.49 (s), –$\mathrm{COOCH_3}$.

Alkyl Acetates LM$_n$: The retention times of LM$_n$ (n=1—4), measured using a 4.0 m column at 140 °C, and of LM$_n$ (n=5—7), measured using a 2.25 m column at 240 °C, agreed with those of authentic acetates as follows (LM$_n$, retention time, referred to acetate, and its retention time): LM$_1$, 1.66, propyl, 1.57; LM$_2$, 4.07, pentyl, 4.09; LM$_3$, 10.20, heptyl, 10.11; LM$_4$, 25.39, nonyl, 25.34; LM$_5$, 2.76, undecyl, 2.80; LM$_6$, 4.87, tridecyl, 4.90; LM$_7$, 8.44, pentadecyl, 8.50. The retention times of tridecyl and pentadecyl acetates were estimated using the relation between the retention times and the number of carbon atoms in the homologues. The mass spectra of LM$_n$ (n=1—7) also supported the above identification.

Methyl α-Branched Alkanoates BA$_n$: The retention times of BA$_n$ (n=1—5), measured using a 4.0 m column at 140 °C, agreed with those of authentic esters as follows (BA$_n$, retention time, referred methyl ester, and its retention time): BA$_1$, 2.86, 2-ethylbutanoate, 2.79; BA$_2$, 6.22, 2-ethylhexanoate, 6.17; BA$_3$, 13.16, 2-butylhexanoate, 13.10; BA$_4$, 14.70, 2-ethyloctanoate, 14.74; BA$_5$, 31.08, 2-butyloctanoate, 30.9. The retention time of methyl 2-butyloctanoate was estimated from those of the homologues. The IR and NMR spectra of BA$_n$ (n=1—3), which were collected by preparative glc, and the mass spectra of BA$_n$ (n=1—4) also supported the above identification. The signals in the NMR spectra were as follows (signal, τ value and assignment): a, 9.10—9.15 (t), $\mathrm{CH_3}$–; b, 8.56—8.74 (m), –$\mathrm{CH_2}$–; c, 7.82—7.87 (m), $>\mathrm{CHCOO}$–; d, 6.38—6.47 (s), –$\mathrm{COOCH_3}$.

α-Branched Alkyl Acetates BM$_n$: The retention times of BM$_1$, measured using a 2.25 m column at 80 °C, and of BM$_2$ and BM$_3$, measured using a 4.0 m column at 150 °C, agreed with those of authentic acetates as follows (BM$_n$, retention time, referred acetate, and its retention time): BM$_1$, 8.12, 1-ethylpropyl, 8.19; BM$_2$, 5.53, 1-ethylpentyl, 5.52; BM_3, 11.30, 1-butylpentyl, 11.31. BM_2 and BM_3 were also confirmed by mass spectrometry. The nonan-5-ol (with a retention time of 9.92 min at 150 °C using a 4.0 m column) in the neutral fraction was detected by glc, as were the alcohols corresponding to LM_n (n=1—7) and BM_n (n=1—3).

Hydrocarbons: The retention times of the e_1—e_4 peaks and of the e_5—e_7 peaks were measured at 140 °C with a 4.0m column and at 240 °C with a 2.25 m column respectively. The retention times and the *m/e* of the parent ion peaks of the components of the e_n peaks (n=1—7) were as follows (e_n, retention time, *m/e* of parent ion peak, and n in $CH_3(CH_2CH_2)_nH$): e_1, 1.13, 128, 4; e_2, 2.85, 156, 5; e_3, 7.02, 184, 6; e_4, 17.48, 212, 7; e_5, 2.17, 240, 8; e_6, 3.74, 268, 9; e_7, 6.50, —, 10.

Methyl α-Cyanoalkanoates N_n and B_n: The retention times of N_n (n=1—3) and B_n (n=1—5) at 190 °C agreed with those of authentic esters as follows (N_n or B_n, retention time, referred to methyl ester, and its retention time): N_1, 0.97, 2-cyanobutanoate, 0.96; N_2, 2.24, 2-cyanohexanoate, 2.24; N_3, 5.44, 2-cyanooctanoate, 5.45; B_1, 1.56, 2-cyano-2-ethylbutanoate, 1.57; B_2, 3.33, 2-cyano-2-ethylhexanoate, 3.32; B_3, 6.74, 2-butyl-2-cyanohexanoate, 6.72; B_4, 7.87, 2-cyano-2-ethyloctanoate, 7.85; B_5, 15.84, 2-butyl-2-cyanooctanoate, 15.83. The mass spectra of N_n (n=1—3) and B_n (n=1—5) also supported the above identification.

Propyl (1.18 min at 190 °C) and pentyl (2.97 min at 190 °C) cyanoacetates could not be detected by glc. Methyl 2-cyano-3-methyl-2-butenoate which had been collected by the use of a silica-gel-column with benzene was confirmed by elemental analysis, and by a study of its IR, NMR, and mass spectra.

Gas Chromatographic Analysis of Products. The gas chromatographic analysis of the telomerization products of methyl acetate with ethylene was made on a 2.25m colum (PEG-20M, 30%). The column temperature was programed to rise at a rate of 4 °C/min from 80 °C to 240 °C. The amounts of the telomers relative to those of methyl 2-ethylhexanoate were determined by the use of calibration curves. The analysis of the telomerization products of methyl cyanoacetate with ethylene was made on a 2.25 m, column (Apiezone Grease L, 30%). The column temperature was programed to rise at a rate of 4 °C/min from 140 °C to 240 °C. Cyclododecane was used as the internal standard.

Determination of the Relative Ratios (M/A). Methyl acetate was removed from the reaction mixture of the telomerization of methyl acetate with ethylene by the use of a spinning-band column. The NMR spectra of the residues were measured in carbon tetrachloride.

The decomposition of DTBP (3.7 g) in methyl acetate (74 g) was carried out in an autoclave. The treatment of the reaction mixture was similar to that described above. The reaction of 1-octene (5.6 g) with methyl acetate (74 g) in the presence of DTBP was carried out much like the telomerization procedure. The ratio of the yield of nonyl acetate to that of methyl decanoate was determined by glc. In the experiments at 20 °C, the reaction mixture was irradiated with a high-pressure mercury lamp (UM-102).

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