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CHROMATOGRAPHY OF MONOMERS

V. TEMPERATURE-PROGRAMMED GLASS CAPILLARY GAS CHROMATOGRAPHIC SEPARATION AND GAS CHROMATOGRAPHY–MASS SPECTROMETRIC IDENTIFICATION OF A MIXTURE OF C_1–C_{18} ALKYL ESTERS OF ACRYLIC AND METHACRYLIC ACIDS

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SUMMARY

The possibilities for the separation of a mixture of aliphatic C_1–C_{18} alkyl esters of acrylic and methacrylic acids have been studied on glass capillary columns with non-polar (OV-101 and SE-54) and polar (SP-1000) phases under temperature-programmed conditions. The electron impact and methane and isobutane chemical ionization mass spectra of 38 acrylate and methacrylate monomers are reported and their use for identification purposes is discussed.

INTRODUCTION

Esters of methacrylic and acrylic acid are commonly used as monomers in the manufacture of polymeric materials. The structure and amount of the monomers will influence the properties of the polymers. Thus there is a need for suitable methods for characterizing the products. Moreover, because of the high toxicity of these monomers it is necessary to control their concentrations. The most suitable technique for the determination of both the acrylates and methacrylates seems to be gas chromatography (GC), especially capillary GC combined with mass spectrometry (MS).

There are no reports in the literature of the simultaneous GC separation of a mixture of C_1–C_{18} alkyl esters of acrylic and methacrylic acids, but chromatographic methods of determining individual acrylic compounds have been described[1]. GC–MS has been used to separate and identify the monomers[2]. In particular, MS has proved to be useful for the identification of the various acrylates and methacrylates in many polymeric materials[3,4].

In this work, polar (SP-1000) and non-polar (OV-101, SE-54) glass capillary columns were used in an attempt to find the most suitable operating conditions for simultaneous determination of aliphatic C_1–C_{18} alkyl esters of acrylic and methacrylic acids. The use for identification purposes of electron impact (EI) and methane

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and isobutane chemical ionization (CI) mass spectra of all the 38 acrylate and methacrylate monomers is discussed.

EXPERIMENTAL

Samples

The esters, either prepared in the laboratory or of commercial origin, were characterized as previously reported[5,6].

Gas chromatography

GC analyses were carried out on a Varian Model 3700 instrument equipped with a flame ionization detector under the following operating conditions: injector and detector temperatures, 300°C, carrier gas, nitrogen with a splitting ratio of *ca.* 1:100; chart speed, 10 mm/min. The glass capillary columns were a laboratory-made OV-101 (19 m × 0.28 mm I.D.), an SE-54 (30 m × 0.24 mm I.D.) supplied by Supelco (Bellefonte, PA, U.S.A.) and an SP-1000 (46 m × 0.23 mm I.D.) supplied by SGE (North Melbourne, Australia). The column temperature was 50°C for the first 3 min and then programmed from 50°C to 210°C (OV-101 and SP-1000) or from 50°C to 230°C (SE-54) at 10, 15, or 20°C/min and held at the final temperature until peak elution had ceased.

The retention times were measured from the time of sample injection by a reporting integrator Autolab System IV (Spectra-Physics, Mountain View, CA, U.S.A.) with a precision of 0.1 s. The values of the retention times presented were calculated from two to four measurements with good reproducibility.

Gas chromatography–mass spectrometry

GC–MS data were recorded on a Varian MAT 44 S quadrupole mass spectrometer connected to a Varian Model 3700 gas chromatograph and equipped with the dual EI/CI ion source. A glass capillary column (20 m × 0.30 mm I.D.) containing SE-54 was employed. The operating conditions were: injector temperature 200 and 300°C, respectively, for the higher alkyl esters; open split coupling and line-of-sight inlet temperatures, 200°C; helium carrier gas flow-rate *ca.* 1 ml/min; the splitting ratio 1:50. For the separation of homologous series various programmed column temperatures were used in order that representative mass spectra could be taken.

In the EI mode the electron ionizing energy was 70 eV and the ion source temperature 160–175°C. Mass numbers from *m/z* 15 to 350 were recorded.

In the CI mode isobutane (0.9995) and methane (0.99995), both supplied by Messer Griesheim (Düsseldorf, F.R.G.), were employed as reagent gases at an ion source pressure of *ca.* 40 Pa and an electron ionizing energy of 200 eV. The CI mass spectra were recorded over the ranges *m/z* 60–350 and 60–700, respectively, for observing $[2M + 1]^+$ adduct ions. With methane the ion source temperature was 160–170°C. In the case of isobutane reagent gas, mass spectra were recorded at two different source temperatures, 160–170°C and 210–220°C, respectively.

In both EI and CI modes, spectra were acquired at the rate of *ca.* 40 per min and were taken in the maximum of overloaded chromatographic peaks to ensure approximately constant sample pressure in the ion source during the scanning period.

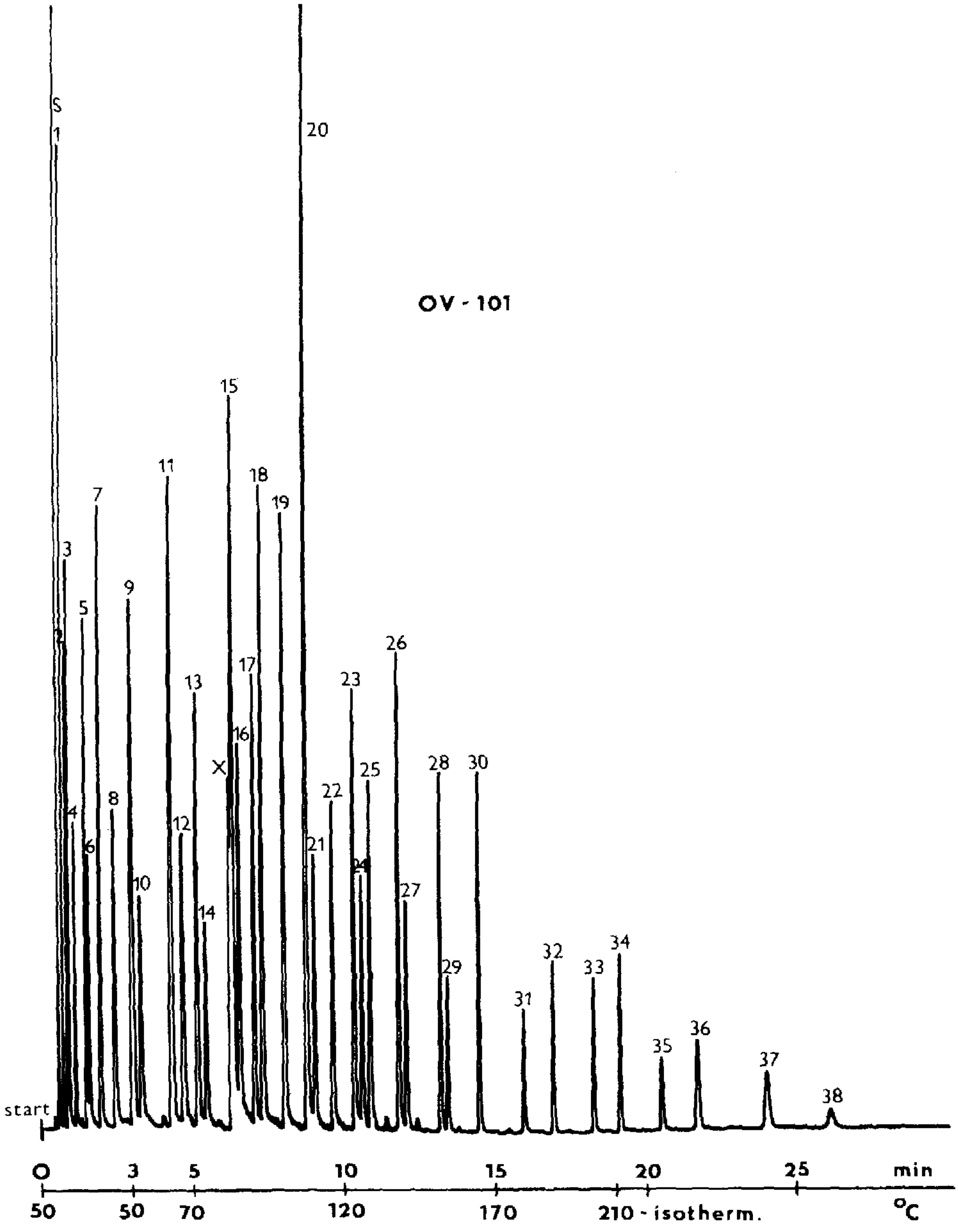

Fig. 1. Chromatogram of a mixture of 38 acrylates and methacrylates separated on an OV-101 glass capillary column, operated at 50°C for 3 min and programmed to 210°C at 10°C/min, then isothermally at 210°C until elution of peaks had ceased. For peak identification, see Table I; S = solvent; X = 2-ethylhexanol.

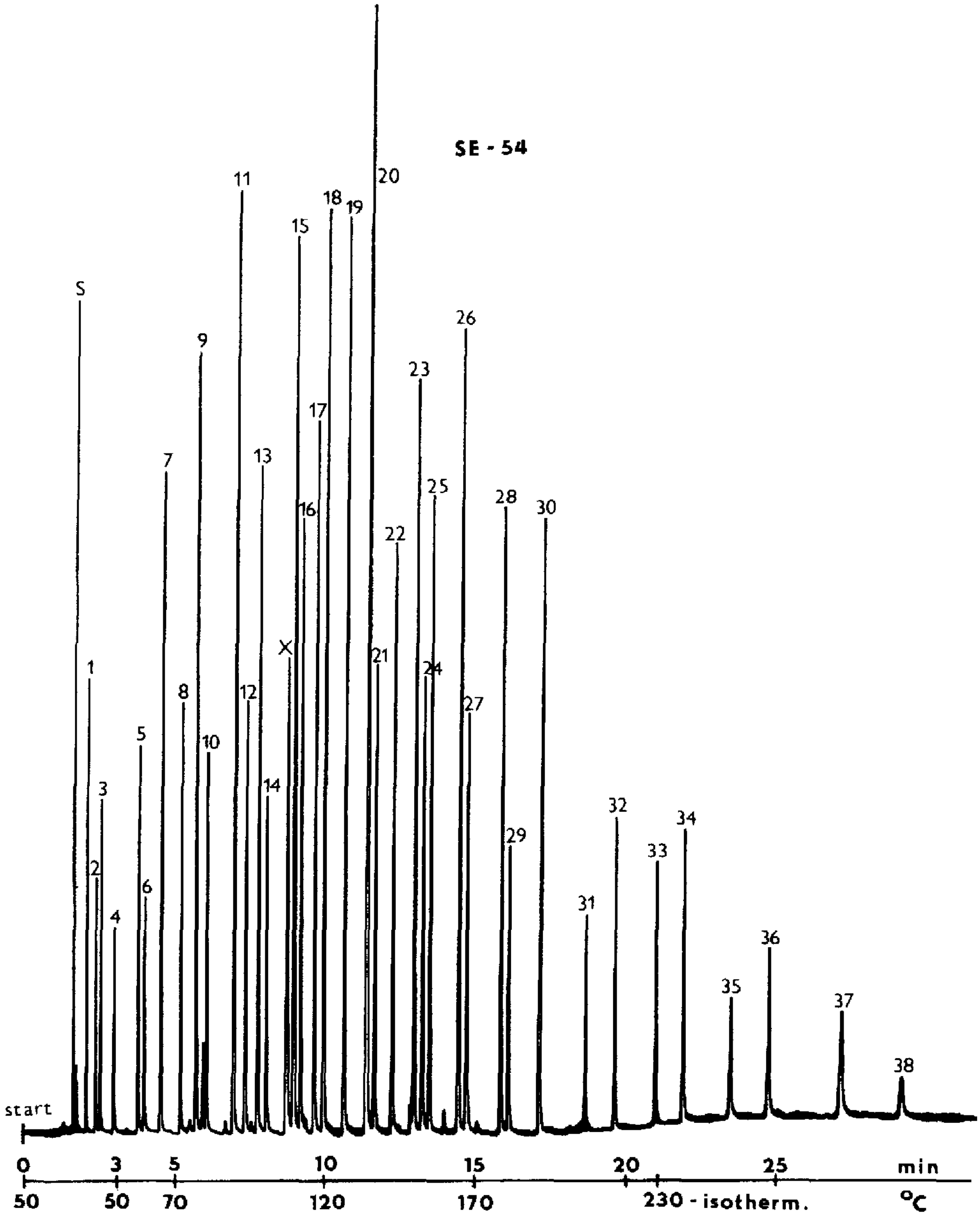

Fig. 2. Chromatogram of a mixture of 38 acrylates and methacrylates separated on an SE-54 glass capillary column, operated at 50°C for 3 min and programmed to 230°C at 10°C/min, then isothermally at 230°C until elution of peaks had ceased. For peak identification see Table II; S = solvent; X = 2-ethylhexanol.

RESULTS AND DISCUSSION

The chromatograms illustrated in Figs. 1–3 show the separation of the mixture of C_1–C_{18} alkyl esters of acrylic and methacrylic acids under optimum operating

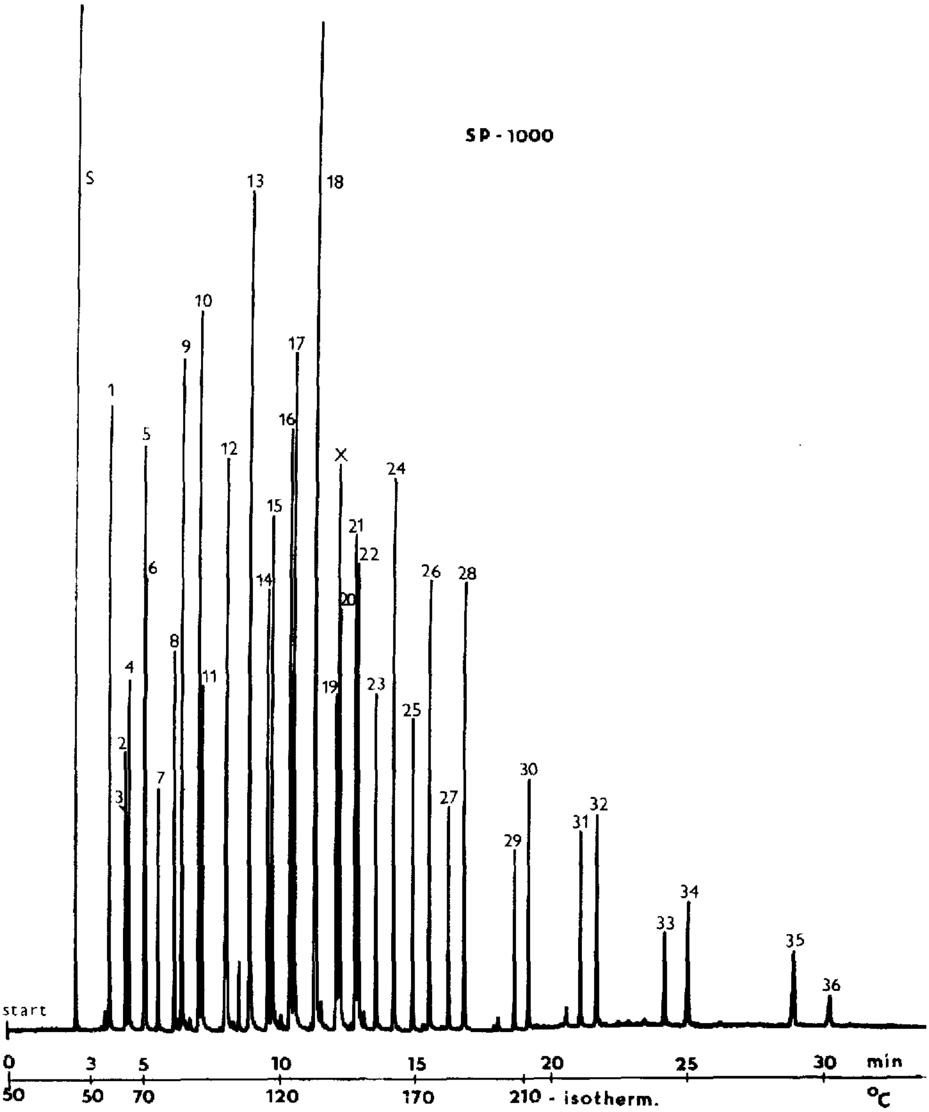

Fig. 3. Chromatogram of a mixture of 38 acrylates and methacrylates separated on an SP-1000 glass capillary column, operated at 50°C for 3 min and programmed to 210°C at 10°C/min, then isothermally at 210°C until elution of peaks had ceased. For peak identification see Table III; S = solvent; X = 2-ethylhexanol.

conditions. Tables I–III give the retention data for all the 38 monomers, analysed using three different programmed temperatures on OV-101, SE-54 and SP-1000 glass capillary columns. On all the stationary phases, the relative retention times for *n*-hexyl acrylate are taken as 1.00.

Owing to the wide range of relative molecular masses in the complex mixture of monomers it was necessary to use temperature programming with a high temper-

TABLE I

RETENTION TIMES (t_R) AND RELATIVE RETENTION TIMES (RRT) ON OV-101

For aliphatic C_1–C_{18} *n*-alkyl acrylates (A1–A18) and methacrylates (M1–M18), C_3–C_6 isoalkyl acrylates (iA3–iA6) and methacrylates (iM3–iM6), 2-ethylhexyl acrylate (EHA) and methacrylate (EHM).

Peak No. in Fig. 1	*Compound*	*Rate of temperature increase*					
		10°C/min		*15°C/min*		*20°C/min*	
		$t_R(s)$	*RRT*	$t_R(s)$	*RRT*	$t_R(s)$	*RRT*
1	A1	46.4	0.10	46.2	0.12	46.2	0.13
2	A2	54.1	0.12	53.8	0.14	53.8	0.15
3	M1	58.6	0.13	58.3	0.15	58.3	0.16
4	iA3	70.7	0.16	69.8	0.18	70.3	0.19
5	M2	92.6	0.21	91.9	0.23	91.9	0.25
6	A3	98.3	0.22	97.7	0.25	97.6	0.27
7	iM3	121.0	0.27	120.2	0.30	119.9	0.33
8	iA4	149.7	0.34	148.9	0.38	148.4	0.41
9	M3	183.9	0.42	182.9	0.46	182.3	0.50
10	A4	201.3	0.45	200.0	0.51	198.9	0.55
11	iM4	262.5	0.59	254.7	0.65	248.7	0.68
12	iA5	284.0	0.64	272.6	0.69	264.3	0.73
13	M4	312.5	0.71	295.8	0.75	284.0	0.78
14	A5	330.0	0.75	309.8	0.78	295.5	0.81
15	iM5	384.9	0.87	351.1	0.89	330.0	0.91
16	iA6	397.4	0.90	361.4	0.92	337.7	0.93
17	M5	426.1	0.96	382.5	0.97	354.5	0.97
18	A6	442.8	1.00	394.7	1.00	364.1	1.00
19	iM6	486.2	1.10	426.4	1.08	389.2	1.07
20	M6	529.8	1.20	457.0	1.16	412.9	1.13
21	A7	545.5	1.23	467.8	1.19	421.3	1.16
22	EHA	581.4	1.31	493.0	1.25	440.9	1.21
23	M7	623.8	1.41	522.2	1.32	463.3	1.27
24	A8	639.0	1.44	532.6	1.35	471.3	1.29
25	EHM	655.2	1.48	544.0	1.38	480.2	1.32
26	M8	711.2	1.61	582.3	1.48	509.4	1.40
27	A9	725.9	1.64	592.3	1.50	517.0	1.42
28	M9	793.0	1.79	637.9	1.62	552.0	1.52
29	A10	806.8	1.82	647.5	1.64	559.2	1.54
30	M10	869.9	1.96	690.7	1.75	592.4	1.63
31	A12	956.2	2.16	749.1	1.90	636.8	1.75
32	M12	1013.0	2.29	787.6	2.00	666.1	1.83
33	A14	1091.4	2.46	841.7	2.13	713.6	1.96
34	M14	1142.7	2.58	884.2	2.24	753.3	2.07
35	A16	1225.5	2.77	961.1	2.44	828.0	2.27
36	M16	1296.7	2.93	1030.9	2.61	859.7	2.36
37	A18	1434.5	3.24	1165.7	2.95	1027.9	2.82
38	M18	1559.1	3.52	1288.8	3.27	1149.9	3.16

ature rise of 10, 15 or 20°C/min, giving short analysis times and sharp peaks for long-chain esters. On the other hand, a sufficiently low initial temperature, 50°C, is required for the volatile compounds to be separated from the hexane solvent peak. The best separation of volatile esters of acrylic and methacrylic acids from the hexane peak was on the polar SP-1000 phase (Fig. 3 and Table III).

TABLE II

RETENTION TIMES AND RELATIVE RETENTION TIMES ON SE-54

For aliphatic C_1–C_{18} *n*-alkyl acrylates (A1–A18) and methacrylates (M1–M18), C_3–C_6 isoalkyl acrylates (iA3–iA6) and methacrylates (iM3–iM6), 2-ethylhexyl acrylate (EHA) and methacrylate (EHM).

Peak No. in Fig. 2	*Compound*	*Rate of temperature increase*					
		10°C/min		*15°C/min*		*20°C/min*	
		$t_R(s)$	*RRT*	$t_R(s)$	*RRT*	$t_R(s)$	*RRT*
1	A1	125.7	0.21	125.2	0.24	125.7	0.27
2	A2	144.9	0.24	144.0	0.28	145.0	0.31
3	M1	155.0	0.26	153.8	0.30	154.9	0.33
4	iA3	181.5	0.30	179.9	0.35	181.6	0.39
5	M2	229.5	0.38	225.7	0.44	225.0	0.48
6	A3	241.6	0.40	236.5	0.46	235.1	0.50
7	iM3	274.6	0.46	265.6	0.51	261.6	0.56
8	iA4	314.2	0.52	299.6	0.58	291.9	0.62
9	M3	349.0	0.58	328.3	0.64	316.5	0.67
10	A4	366.1	0.61	342.1	0.66	328.4	0.70
11	iM4	419.8	0.70	384.4	0.74	363.9	0.77
12	iA5	442.2	0.74	401.7	0.78	378.2	0.81
13	M4	468.9	0.78	421.9	0.82	394.6	0.84
14	A5	486.4	0.81	434.9	0.84	405.2	0.86
15	iM5	539.9	0.90	474.5	0.92	436.8	0.93
16	iA6	553.1	0.92	484.1	0.94	444.4	0.95
17	M5	580.2	0.97	503.5	0.97	459.5	0.98
18	A6	598.6	1.00	516.7	1.00	469.8	1.00
19	iM6	640.5	1.07	546.5	1.06	493.4	1.05
20	M6	684.4	1.14	577.3	1.12	517.0	1.10
21	A7	699.8	1.17	587.9	1.14	525.3	1.12
22	EHA	734.9	1.23	612.4	1.19	544.4	1.16
23	M7	777.8	1.30	642.1	1.24	567.3	1.21
24	A8	793.9	1.33	653.2	1.26	575.8	1.23
25	EHM	808.6	1.35	663.6	1.28	584.0	1.24
26	M8	866.8	1.45	703.5	1.36	614.7	1.31
27	A9	882.5	1.47	714.4	1.38	623.5	1.33
28	M9	950.5	1.59	761.1	1.47	658.8	1.40
29	A10	965.4	1.61	771.3	1.49	666.4	1.42
30	M10	1029.9	1.72	815.8	1.58	700.6	1.49
31	A12	1119.0	1.87	876.1	1.70	748.2	1.59
32	M12	1176.3	1.97	915.8	1.77	782.7	1.67
33	A14	1258.2	2.10	978.6	1.89	838.3	1.73
34	M14	1313.0	2.19	1026.8	1.99	884.0	1.88
35	A16	1406.7	2.35	1112.6	2.15	965.1	2.05
36	M16	1483.1	2.48	1185.1	2.29	1035.1	2.20
37	A18	1628.0	2.72	1324.4	2.56	1173.7	2.50
38	M18	1749.4	2.92	1444.1	2.79	1290.3	2.75

On both the non-polar OV-101 and SE-54 capillary columns (Figs. 1 and 2, Tables I and II) complete resolution of all the 38 acrylates and methacrylates was achieved: the better separation was on SE-54 column. However, the polar SP-1000 column gave two complete overlaps, *viz.*, isopentyl acrylate (iA5) with butyl meth-

TABLE III

RETENTION TIMES AND RELATIVE RETENTION TIMES ON SP-1000

For aliphatic C_1–C_{18} *n*-alkyl acrylates (A1–A18) and methacrylates (M1–M18), C_3–C_6 isoalkyl acrylates (iA3–iA6) and methacrylates (iM3–iM6), 2-ethylhexyl acrylate (EHA) and methacrylate (EHM).

Peak No. in Fig. 3	*Compound*	*Rate of temperature increase*					
		10°C/min		*15°C/min*		*20°C/min*	
		$t_R(s)$	*RRT*	$t_R(s)$	*RRT*	$t_R(s)$	*RRT*
1	A1	225.6	0.36	226.5	0.40	226.0	0.43
2	A2	259.3	0.41	258.6	0.46	256.4	0.49
3	iA3	264.7	0.42	263.4	0.47	260.8	0.50
4	M1	267.6	0.42	266.3	0.47	263.4	0.51
5	iM3	301.3	0.47	296.3	0.53	291.0	0.56
6	M2	303.6	0.48	298.5	0.53	293.1	0.56
7	A3	331.9	0.52	323.6	0.58	315.8	0.61
8	iA4	367.8	0.58	354.1	0.63	343.1	0.66
9	M3	385.1	0.61	368.5	0.66	355.8	0.68
10	iM4	423.9	0.67	400.4	0.71	383.6	0.74
11	A4	430.3	0.68	405.8	0.72	388.2	0.75
12	iA5≡M4	484.6	0.76	448.8	0.80	425.1	0.82
13	iM5≡A5	536.2	0.85	488.5	0.87	459.0	0.88
14	iA6	574.8	0.91	518.0	0.92	484.0	0.93
15	M5	584.9	0.92	525.3	0.93	490.1	0.94
16	iM6	625.9	0.99	555.9	0.99	515.5	0.99
17	A6	634.5	1.00	562.1	1.00	520.4	1.00
18	M6	682.5	1.08	597.1	1.06	549.1	1.06
19	A7	727.3	1.15	629.7	1.12	576.5	1.11
20	EHA	735.2	1.16	635.0	1.13	579.5	1.11
21	M7	770.0	1.21	660.0	1.17	599.5	1.15
22	EHM	776.1	1.22	664.3	1.18	602.9	1.16
23	A8	814.5	1.28	691.4	1.23	624.3	1.20
24	M8	854.7	1.35	719.2	1.28	646.2	1.24
25	A9	897.1	1.41	749.0	1.33	665.5	1.28
26	M9	934.4	1.47	774.9	1.38	690.3	1.33
27	A10	974.3	1.54	803.1	1.43	713.5	1.37
28	M10	1010.0	1.59	827.8	1.47	734.1	1.41
29	A12	1120.0	1.77	908.8	1.62	803.6	1.54
30	M12	1151.3	1.81	934.0	1.66	826.1	1.59
31	A14	1264.2	1.99	1031.5	1.84	914.0	1.76
32	M14	1300.5	2.05	1063.5	1.89	944.0	1.81
33	A16	1450.1	2.29	1202.0	2.14	1076.0	2.07
34	M16	1502.3	2.37	1251.0	2.23	1123.0	2.16
35	A18	1734.8	2.73	1476.0	2.63	1342.5	2.58
36	M18	1813.0	2.86	1551.5	2.76	1417.0	2.72

acrylate (M4) gave peak 12 and isopentyl methacrylate (iM5) with pentyl acrylate (A5) gave peak 13. In spite of various operating conditions being tried these two pairs of overlapping compounds pairs were not satisfactorily separated. For this reason the SP-1000 capillary column may be considered unsuitable for the complete resolution of the studied mixture of acrylates and methacrylates.

It is generally known that on a polar phase the order of elution is influenced

TABLE IV

EI MASS SPECTRA

For C_1–C_{18} *n*-alkyl (A1–A18), C_3–C_6 isoalkyl (iA3–iA6) and 2-ethylhexyl (EHA) esters of acrylic acid, and C_1–C_{18} *n*-alkyl (M1–M18), C_3–C_6 isoalkyl (iM3–iM6) and 2-ethylhexyl (EHM) esters of methacrylic acid ($m/z \geqslant 39$, relative intensity $\geqslant 5\%$).

Compound	*m/z (relative intensity, %)*
A1	55(100), 42(13), 85(11), 58(9), 43(5)
A2	55(100), 56(14), 45(10), 54(8), 43(7), 73(5), 58(5), 99(5)
A3	55(100), 73(49), 42(13), 54(10), 43(8), 56(6), 85(6), 72(5)
A4	55(100), 56(53), 73(31), 41(21), 54(10), 57(5), 39(5), 85(5)
A5	55(100), 70(46), 73(30), 42(28), 41(16), 54(10), 43(9), 69(9), 56(6), 39(5)
A6	55(100), 56(56), 73(29), 43(25), 84(21), 41(21), 69(12), 85(6), 39(5)
iA3	55(100), 43(37), 73(26), 41(19), 59(13), 42(11), 56(9), 99(9), 39(8)
iA4	55(100), 56(57), 41(18), 73(10), 39(8), 57(6), 85(6)
iA5	55(100), 70(42), 41(17), 43(15), 42(14), 73(9), 39(8), 56(7), 69(5)
iA6	55(100), 43(38), 84(31), 56(24), 41(21), 69(21), 42(14), 39(9), 85(9)
A7	55(100), 56(53), 70(29), 73(29), 41(28), 42(18), 43(17), 98(15), 69(15), 57(13), 39(6), 54(5), 68(5)
A8	55(100), 56(42), 41(33), 43(30), 73(29), 70(25), 42(22), 69(18), 83(17), 84(16), 57(12), 112(8), 82(7), 39(6), 54(5); 68(5), 71(5), 85(5)
A9	55(100), 56(47), 43(38), 41(34), 73(28), 70(22), 69(19), 42(18), 57(13), 83(13), 84(12), 97(11), 98(10), 54(6), 68(6), 39(5), 71(5), 82(5), 126(5)
A10	55(100), 43(42), 56(41), 41(35), 73(28), 70(23), 69(22), 57(19), 42(17), 83(16), 84(12), 97(10), 82(7), 68(7), 54(7), 71(6), 98(5), 39(5), 111(5), 140(5)
A12	55(100), 43(47), 56(39), 69(37), 73(35), 41(33), 57(33), 70(31), 83(25), 97(22), 84(15), 42(13), 82(13), 111(12), 127(11), 98(10), 113(10), 68(10), 71(10), 85(8), 54(7), 112(6)
A14	55(100), 43(52), 57(42), 69(41), 56(39), 41(38), 83(37), 73(35), 70(28), 97(24), 71(17), 127(15), 113(15), 111(14), 82(14), 84(14), 42(13), 68(11), 98(9), 85(8), 96(7), 125(6), 110(5), 112(5), 114(5)
A16	55(100), 43(61), 57(49), 41(42), 69(37), 56(33), 73(31), 83(29), 70(24), 97(21), 71(15), 42(13), 82(13), 84(11), 68(11), 111(10), 127(10), 113(10), 85(9), 54(9), 67(8), 98(8), 96(6), 81(5), 114(5)
A18	55(100), 43(68), 57(56), 83(33), 56(32), 73(31), 41(29), 97(26), 70(22), 71(19), 42(12), 113(12), 84(11), 82(11), 127(11), 69(10), 85(10), 54(10), 111(9), 96(9), 68(8), 114(8), 98(6), 67(6), 125(5), 99(5)
EHA	55(100), 70(52), 41(37), 57(33), 43(25), 56(25), 42(15), 83(14), 69(10), 39(9), 71(9), 84(9), 112(8), 54(6), 58(6), 73(6), 85(6)
M1	41(100), 69(72), 39(45), 100(29), 40(15), 99(11), 59(7), 55(6), 42(6), 85(5)
M2	41(100), 69(100), 39(35), 86(14), 99(14), 40(13), 42(11), 68(11), 45(11), 70(8), 114(6)
M3	69(100), 41(99), 87(63), 39(31), 43(24), 42(23), 40(10), 59(9), 70(5), 86(5), 68(5)
M4	41(100), 69(83), 56(60), 87(55), 39(27), 55(12), 40(9), 57(7), 43(7), 42(6)
M5	41(100), 69(80), 87(61), 70(56), 42(50), 43(38), 55(34), 39(29), 40(10)
M6	69(100), 41(98), 56(67), 87(64), 43(50), 42(33), 55(33), 84(30), 39(25), 40(9), 70(6), 57(5)
iM3	41(100), 43(93), 69(66), 39(37), 87(27), 42(21), 59(20), 40(11), 70(9), 45(6)
iM4	41(100), 69(89), 56(64), 39(33), 87(22), 57(12), 40(10), 42(9), 43(7), 70(6), 55(5)
iM5	41(100), 70(97), 69(78), 55(53), 43(43), 42(35), 39(34), 87(15), 40(10), 71(8)
iM6	69(100), 41(80), 84(50), 43(41), 56(25), 39(24), 55(22), 42(18), 70(9), 40(7), 87(6), 85(5)
M7	41(100), 69(60), 56(46), 87(39), 70(31), 55(30), 39(29), 43(24), 42(22), 57(18), 98(16), 40(9), 68(6)
M8	41(100), 69(63), 87(39), 43(36), 56(34), 70(31), 55(30), 39(26), 42(24), 57(14), 84(13), 83(13), 112(10), 40(8), 68(6), 71(6), 82(5)
M9	41(100), 69(64), 43(47), 56(41), 87(40), 55(36), 70(28), 39(25), 42(20), 57(14), 83(14), 84(12), 97(12), 40(8), 98(8), 68(7), 126(7), 71(6), 88(6)
M10	41(100), 69(61), 43(49), 55(41), 87(41), 56(35), 70(30), 39(23), 57(21), 42(20), 83(18), 97(12), 84(11), 68(8), 88(8), 40(7), 71(6), 82(6), 54(5), 98(5), 111(5)

(Continued on p. 98)

TABLE IV (*continued*)

Compound	*m/z (relative intensity, %)*
M12	41(100), 69(59), 43(48), 87(44), 55(36), 70(32), 57(28), 56(28), 83(22), 97(19), 39(15), 42(15), 88(13), 84(12), 71(10), 68(8), 40(8), 82(8), 111(8), 98(7), 54(5), 96(5), 67(5), 168(5), 85(5)
M14	41(100), 69(61), 87(58), 43(57), 55(40), 57(37), 70(31), 83(28), 56(25), 97(23), 88(19), 71(15), 42(14), 39(13), 84(12), 111(11), 82(11), 68(9), 40(7), 98(7), 96(6), 54(6), 67(6), 85(6), 125(5)
M16	41(100), 69(88), 43(86), 57(73), 55(66), 87(62), 83(43), 56(37), 70(36), 97(35), 88(33), 71(25), 42(18), 39(16), 82(15), 84(14), 111(12), 68(11), 54(10), 96(10), 98(9), 67(8), 40(8), 125(6), 58(5), 81(5), 113(5)
M18	41(100), 43(89), 69(77), 55(67), 87(62), 57(58), 83(39), 88(37), 97(34), 56(32), 70(31), 71(24), 42(19), 68(15), 111(15), 82(14), 39(13), 85(13), 84(12), 54(11), 67(11), 96(11), 98(8), 40(7), 81(7), 113(6), 125(6), 127(5)
EHM	41(100), 70(75), 69(70), 55(35), 57(28), 43(27), 39(25), 56(24), 42(16), 83(16), 112(15), 71(12), 84(11), 40(8), 87(8)

more by the structures of compounds than by their boiling points. So the most interested feature of the retention behaviour of the studied monomers on the SP-1000 phase is the elution of isopropyl methacrylate before ethyl methacrylate. The retention index values for these two compounds on the same SP-1000 capillary column[6] and those published by Ashes and Haken[7] on the XF-1150 phase of similar polarity indicate the same elution sequence.

It may be concluded that the retention order of aliphatic C_1–C_{18} alkyl esters of acrylic and methacrylic acids under temperature programming presented herein is consistent with the retention index sequence determined on the same OV-101, SE-54 and SP-1000 capillary columns under isothermal conditions[6].

The EI and methane and isobutane CI mass spectral data of all the studied monomers are listed in Tables IV–VI.

The EI spectra of all the acrylates (Table IV) show a prominent cleavage of the alkoxy group from the molecular ion, giving the acryloyl ion, *m/z* 55, as the base peak. With the exception of methyl and isohexyl esters, an intense fragment ion at *m/z* 73, corresponding to the loss of the alkyl group and formation of a protonated acrylic acid ion, is observed with all acrylates.

The EI spectra of the aliphatic methacrylates studied (Table IV) show the most prominent peaks at *m/z* 69, due to the methacryloyl ion $CH_2=C/CH_3/CO^+$, and at *m/z* 41, due to $C_3H_5^+$ ion. In the EI spectra of C_1–C_{18} alkyl methacrylates, the *m/z* 41 peak is the base peak or the second most intense one. With the exception of methyl and ethyl methacrylates, an *m/z* 87 ion is present in all the EI spectra of methacrylates. Parallel to the *m/z* 73 ion in the acrylates, as expected, the *m/z* 87 ion is most probably the protonated methacrylic acid ion.

Methane CI spectra of acrylates and methacrylates are listed in Table V. For C_3–C_{18} *n*-alkyl and 2-ethylhexyl esters of acrylic acid, the methane spectra exhibit a base peak at *m/z* 73 due to the protonated acrylic acid ion. However, in the spectrum of ethyl acrylate, this peak is only of 25% relative intensity and in the spectrum of methyl acrylate it is absent.

With the exception of the methyl ester, methane CI spectra of the methacrylates studied showed abundant *m/z* 87 ions due to the protonated methacrylic acid. Si-

TABLE V

METHANE CI MASS SPECTRA

For C_1–C_{18} *n*-alkyl (A1–A18), C_3–C_6 isoalkyl (iA3–iA6) and 2-ethylhexyl (EHA) esters of acrylic acid and C_1–C_{18} *n*-alkyl (M1–M18), C_3–C_6 isoalkyl (iM3–iM6) and 2-ethylhexyl (EHM) esters of methacrylic acid ($m/z \geq 60$, relative intensity $\geq 2\%$); m/z values of pseudomolecular ions are italicized.

Compound	*m/z (relative intensity, %)*
A1	*87*(100), 88(5), 85(2)
A2	*101*(100), 73(25), 102(5), 201(3), 100(2)
A3	73(100), *115*(99), 101(12), 116(7), 113(6), 74(3), 100(2), 229(2)
A4	73(100), *129*(49), 101(13), 113(6), 130(4), 74(3), 100(2), 257(2)
A5	73(100), *143*(26), 71(17), 101(10), 69(6), 70(4), 113(4), 74(3), 72(2), 144(2)
A6	73(100), 85(22), *157*(20), 101(14), 83(10), 113(5), 69(4), 84(4), 74(3), 100(2), 158(2)
iA3	73(100), *115*(36), 101(9), 113(5), 74(3), 116(2)
iA4	73(100), *129*(52), 101(20), 113(12), 130(5), 74(3), 100(3), 127(2)
iA5	71(100), *143*(17), 73(13), 101(6), 70(5), 72(5), 69(4), 113(3), 144(2)
iA6	85(100), 73(83), 101(12), *157*(8), 83(7), 84(7), 86(7), 113(7), 69(4), 74(3), 100(2)
A7	73(100), *171*(24), 101(20), 97(17), 99(9), 113(7), 83(6), 98(4), 69(3), 74(3), 100(3), 172(3), 70(2)
A8	73(100), 71(30), 101(16), 111(14), 113(14), *185*(12), 69(7), 97(5), 74(3), 112(3), 72(2), 83(2)
A9	73(100), 71(32), 101(19), 69(17), 85(17), 127(11), 125(10), *199*(10), 83(7), 113(6), 74(3), 111(3), 72(2), 97(2)
A10	73(100), 71(31), 83(29), 101(29), 85(25), 141(13), 69(12), 99(10), 97(8), *213*(8), 113(7), 139(7)
A12	73(100), 101(24), *241*(23), 71(22), 85(21), 97(21), 169(17), 99(14), 111(14), 83(13), 113(12), 167(7), 69(5), 127(4), 74(3), 125(3), 239(3), 242(3), 100(2), 170(2), 281(2)
A14	73(100), *269*(41), 101(32), 197(23), 97(21), 71(18), 111(16), 85(14), 113(14), 83(12), 99(11), 195(10), 125(9), 127(8), 270(8), 267(7), 69(5), 139(4), 141(4), 74(3), 100(3), 198(3), 196(2), 309(4), 297(3)
A16	73(100), 101(37), *297*(35), 225(28), 97(22), 71(17), 111(14), 113(14), 83(13), 85(12), 223(11), 99(9), 125(9), 295(8), 127(7), 139(6), 141(6), 69(5), 153(4), 155(4), 337(5), 325(4)
A18	73(100), *325*(35), 101(33), 253(25), 97(22), 71(15), 83(13), 111(13), 251(13), 85(12), 113(12), 323(12), 125(9), 99(8), 326(7), 139(6), 69(5), 127(5), 153(3), 167(3), 74(2), 141(2), 155(2), 252(2), 324(2)
EHA	73(100), 113(76), 71(47), *185*(33), 101(15), 111(13), 112(7), 369(7), 69(6), 97(6), 114(6), 70(5), 83(3), 186(3), 74(2)
M1	*101*(100), 69(12), 73(11), 102(5), 81(3), 85(3), 100(3)
M2	*115*(100), 87(52), 69(24), 116(7), 114(3)
M3	87(100), *129*(69), 69(35), 115(13), 101(8), 127(5), 130(5)
M4	87(100), *143*(40), 69(31), 115(17), 88(4), 127(4), 144(4)
M5	87(100), 69(38), *157*(26), 71(16), 115(13), 70(6), 88(4), 127(4), 129(3), 158(3)
M6	87(100), 69(39), *171*(24), 115(15), 83(13), 85(13), 84(5), 127(5), 71(4), 88(4), 172(3)
iM3	87(100), *129*(30), 69(14), 115(9), 88(4), 127(4), 101(3), 130(3), 71(2)
iM4	87(100), *143*(40), 69(39), 115(21), 127(8), 88(5), 71(4), 144(3)
iM5	71(100), 69(24), 87(23), *157*(18), 70(9), 115(9), 72(5), 127(3), 129(2)
iM6	85(100), 87(85), 69(34), 115(13), *171*(13), 84(10), 83(8), 86(7), 127(6), 88(4), 71(3)
M7	87(100), 69(31), *185*(20), 97(13), 115(10), 71(4), 88(4), 98(4), 127(4), 70(3), 83(3), 99(3), 186(2)
M8	87(100), 69(32), 71(14), *199*(13), 111(11), 115(10), 88(4), 70(3), 112(3), 113(3), 127(3)
M9	87(100), 69(39), 71(15), *213*(12), 115(10), 125(7), 85(6), 127(6), 83(5), 88(5), 70(3), 126(3)
M10	87(100), 69(32), 83(15), 71(12), 115(12), *227*(9), 85(7), 88(5), 97(5), 139(4), 70(3), 99(3), 127(3), 141(3)
M12	87(100), *255*(38), 69(34), 115(22), 97(15), 71(14), 83(10), 111(10), 85(7), 167(7), 256(6), 88(5), 99(5), 127(5), 169(5), 113(3), 253(3), 70(2), 125(2), 168(2), 295(2)
M14	87(100), *283*(51), 69(37), 115(20), 97(13), 71(10), 111(10), 284(9), 83(8), 195(7), 85(6), 125(6), 127(6), 281(6), 88(5), 99(5), 113(4), 197(4), 139(3), 323(3), 70(2), 89(2), 282(2)

(Continued on p. 100)

TABLE V *(continued)*

Compound	*m/z (relative intensity %)*
M16	87(100), 69(39), *311*(39), 115(18), 97(13), 71(11), 111(8), 223(8), 309(8), 312(8), 83(7), 88(6), 125(6), 85(5), 127(5), 225(4), 70(3), 89(3), 139(3), 310(3), 113(3), 99(3), 153(2), 339(2), 351(2)
M18	87(100), 69(35), *339*(30), 115(14), 97(10), 71(9), 251(8), 111(8), 83(6), 340(6), 88(4), 125(4), 89(3), 127(3), 252(3), 338(3), 337(2), 341(2), 85(2)
EHM	87(100), 113(51), 71(39), 69(34), 115(17), *199*(16), 111(14), 112(10), 127(9), 70(7), 114(7), 97(5), 88(4), 72(3), 83(2)

TABLE VI

ISOBUTANE MASS SPECTRA OF ACRYLATES AND METHACRYLATES AT TWO DIFFERENT ION-SOURCE TEMPERATURES (TSOU)

($m/z \geqslant 60$, relative intensity $\geqslant 2\%$).

Compound	*TSOU (°C)*	*Mol. wt.*	*Relative intensity (%)*			
			$(M+1)^+$	$[CH_2=C(CH_3)COOH_2]^+$	$(CH_2=CHCOOH_2)^+$	$[CH_2=C(CH_3)CO]^+$
A1	155	86	100		–	
A2	156	100	100		–	
A3	158	114	100		4	
A4	162	128	100		6	
A5	166	142	100		8	
A6	156	156	100		3	
iA3	164	114	100		16	
iA4	164	128	100		7	
iA5	164	142	100		–	
iA6	164	156	100		43	
A7	158	170	100		3	
A8	160	184	100		8	
A9	162	198	100		6	
A10	164	212	100		4	
A12	158	240	100		6	
A14	161	268	100		8	
A16	170	296	100		7	
A18	168	324	100		10	
EHA	170	184	41		100	
M1	161	100	100	–		–
M2	161	114	100	–		2
M3	164	128	100	4		3
M4	168	142	100	5		2
M5	170	156	100	6		2
M6	164	170	100	9		3
iM3	164	128	100	33		6
iM4	171	142	100	13		4
iM5	172	156	100	5		5
iM6	174	170	91	60		8
M7	166	184	100	10		2
M8	168	198	100	12		2
M9	170	212	100	12		2
M10	164	226	100	13		2

multaneously with exception of methyl, ethyl, isopentyl and isohexyl esters, all the spectra of the methacrylates showed the *m/z* 87 ion as the base peak. As in the EI spectra, the methacryloyl ion, *m/z* 69, is another common feature of the methane CI mass spectra of aliphatic C_1–C_{18} alkyl esters of methacrylic acid.

Methane CI spectra of acrylates and methacrylates showed protonated molecular ions of medium intensity. For methyl and ethyl esters $(M+1)^+$ ions were the base peaks. A comparison of the two types (EI and methane CI) of mass spectra for aliphatic acrylates and methacrylates showed that the methane CI mass spectra were more informative as they showed both the molecular weight and the compound type.

The isobutane CI mas spectra of C_1–C_{18} alkyl acrylates and methacrylates

$(M+1-CH_2{=}CHCOOH)^+$	$[M+1-CH_2{=}C(CH_3)COOH]^+$	$(2M+1)^+$	*m/z* 113	*m/z* 127	*Additional peaks m/z (relative intensity, %)*
–		3			86(3)
–		3			100(3)
–		3			114(3)
–		3			128(3)
–		–			142(2)
–		10			
–		9			
–		10			
16		5			
72		–			
–		3			170(2)
2		4			71(2)
–		2			71(2)
–		2			
3		7			
5		6			
8		3			
5		–			
83		15			
	–	14			100(6)
	–	13			114(5)
	–	12			128(5)
	–	7			142(6)
	–	–			
	2	8			170(3)
	–	–			
	–	–			
	17	–			70(3)
	100	–			84(5)
	–	4			184(2)
	–	4			71(2)
	–	–			
	–	2			127(2)

(Continued on p. 102)

TABLE VI (*continued*)

Compound	*TSOU (°C)*	*Mol. wt.*	*Relative intensity (%)*			
			$(M+1)^+$	$[CH_2 = C(CH_3)COOH_2]^+$	$(CH_2 = CHCOOH_2)^+$	$[CH_2 = C(CH_3)CO]^+$
M12	168	254	100	33		9
M14	167	282	100	23		4
M16	166	310	100	14		–
M18	171	338	100	16		3
EHM	168	198	68	100		23
A1	218		100		–	
A2	218		100		5	
A3	219		100		20	
A4	221		100		33	
A5	222		100		60	
A6	223		100		84	
iA3	214		80		100	
iA4	216		100		43	
iA5	218		100		8	
iA6	221		14		81	
A7	213		79		100	
A8	215		66		100	
A9	216		45		100	
A10	219		36		100	
A12	220		28		100	
A14	220		34		100	
A16	222		28		100	
A18	222		26		100	
EHA	211		30		100	
M1	217		100	–		–
M2	219		100	–		6
M3	220		100	10		13
M4	222		100	20		11
M5	224		100	36		16
M6	225		100	41		17
iM3	211		100	86		7
iM4	212		100	47		14
iM5	214		100	14		10
iM6	216		22	78		7
M7	216		100	92		18
M8	218		68	100		24
M9	219		51	100		18
M10	221		52	100		17
M12	220		49	100		23
M14	222		42	100		21
M16	225		39	100		16
M18	223		34	100		10
EHM	212		30	100		42

* Both fragment ions of the same *m/z* value.

$(M+1-CH_2=CHCOOH)^+$	*$[M+1-CH_2=C(CH_3)COOH]^+$*	*$(2M+1)^+$*	*m/z 113*	*m/z 127*	*Additional peaks m/z (relative intensity, %)*
	–	–			
	–	–			
	–	–			
	–	–			
	71	–			71(7) 111(8) 112(5) 127(6) 128(6)
–			–		
–			–		87(3)
–			5		
–			4		
4			3		
8			4		
–			2		
–			3		
89			2		
100			–		
7			5		
15*			15*		71(11) 111(4) 187(3)
14			2		71(13) 85(5) 128(5)
16			4		71(13) 83(5) 85(13) 99(3)
18			16		69(4) 71(18) 83(4) 85(12) 97(2) 99(14) 111(4)
26			19		69(6) 71(15) 83(8) 85(9) 97(6) 99(8) 127(6) 141(4) 198(4)
24			22		69(9) 71(27) 83(15) 85(16) 97(13) 99(12) 111(9) 127(9) 141(4)
26			18		69(11) 71(25) 83(13) 85(16) 97(12) 99(8) 111(5) 127(4) 155(4)
72*			72*		70(8) 71(12) 83(3) 112(7) 114(10) 127(5)
	–			–	
	–			–	
	–			2	
	–			3	
	–			2	
	2			3	
	–			–	128(3)
	–			3	142(2)
	49			2	72(3)
	100			–	84(3)
	–			7	71(2) 97(2)
	2			6	71(7) 111(5) 128(3)
	9*			9*	71(5) 83(2) 125(2) 128(2)
	2			4	71(4) 83(6) 85(3)
	–			4	71(4) 83(3) 85(2) 97(3) 111(2)
	–			6	71(6) 83(3) 97(2)
	–			4	71(4) 83(3) 97(2)
	–			–	71(5) 97(2)
	65			3	70(10) 71(13) 86(3) 111(3) 112(7) 128(5) 197(2)

listed in Table VI were recorded at two different ion-source temperatures at approximately unchanged reagent gas pressure. Overall, the isobutane CI mass spectra of the aliphatic esters of acrylic and methacrylic acids are quite simple. At the lower ion-source temperature, with the exception of 2-ethylhexyl and isohexyl methacrylates and 2-ethylhexyl acrylate, all the esters showed the protonated molecular ions as the base peaks. Only relatively weak fragment ions corresponding to the protonated acrylic acid ion for acrylates, and protonated methacrylic acid and methacryloyl ions for methacrylates are visible in the spectra of the majority of the esters. In addition, weak $(2M + 1)^+$ ions are often observed. Comparing the spectra at the two different ion-source temperatures, there is a marked increase in the intensity of the fragment ions at the higher temperature. The higher alkyl chain esters gave the protonated acrylic and methacrylic acid ions, respectively, as the base peaks at the higher temperature.

CONCLUSION

The complete separation of all 38 aliphatic C_1–C_{18} alkyl esters of acrylic and methacrylic acids was achieved on both the non-polar OV-101 and SE-54 capillary columns but not on the polar SP-1000 one.

Of the various MS ionization modes used, the methane CI mode was recognized to be the most useful for identification of the acrylate and methacrylate monomers, because the pseudo-molecular ions were fairly intense and the cleavage give rise to characteristic abundant fragment ions.

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