

# New substituted polymethylenes by free radical polymerization of bulky fumarates and their properties

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## Abstract

The free radical polymerization of fumarates (DRFs) bearing sterically crowded ester groups was investigated. Various new monomers were synthesized and their polymerization behaviour was looked into. In bulk polymerizations at 60°C initiated with 2,2'-azobisisobutyronitrile (AIBN), their polymerization reactivity depends sensitively on the structure of both alkyl ester groups. Besides the polymerization of simple alkyl fumarates, the extension to substituents bearing functional groups was explored. Functional groups have been found to be barely tolerated, successful polymerization requiring the use of particular initiators. The polymers were characterized by <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectroscopies, and wide-angle X-ray diffraction (WAXD), and some thermal properties were examined. © 2000 Elsevier Science Ltd. All rights reserved.

*Keywords:* Dialkyl fumarates; Free radical polymerization; Steric effects

## 1. Introduction

1,2-disubstituted ethylenic monomers are generally thought not to homopolymerize due to the strong steric hindrance of the propagation step by the substituents in both 1- and 2- positions. However, a series of dialkyl fumarates (DRFs) have been reported to polymerize in the presence of radical initiators when bearing bulky alkyl ester groups, yielding polymers of high molar mass [1–7]. For these monomers, increased bulkiness of the ester groups enhances polymerization reactivity, i.e. the polymerization rate and molar mass of the polymer increase. Moreover, the high density of substituents of the resulting poly(alkoxycarbonylmethylene) structures (Fig. 1), combined with the bulkiness of the substituents, intuitively is expected to lead to rather stiff main chains.

A similar polymerization behaviour has been observed for some DRFs with different alkyl ester groups, e.g. for methyl *t*-alkyl fumarates [2,8]. In contrast, the few attempts to polymerize fumarates bearing other than pure alkyl ester

groups, by free radical process, led to low oligomers only, if they reacted at all [9–12].

Here, we describe the preparation of fumarates bearing different alkyl ester groups including functional groups (Table 1), their free radical polymerization using initiators 2,2'-azobisisobutyronitrile (AIBN), dimethyl 2,2'-azobisisobutyrate (MAIB) and potassium persulphate (K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>) and the effects of the substituents on polymerization reactivities, polymer structures and properties.

## 2. Experimental

### 2.1. Materials

All solvents used were analytical grade, or were distilled prior to use. Flash chromatography was performed on silicagel (Merck, 230–400 mesh). Fumaryl chloride was distilled under a reduced pressure before use. Isopropanol, cyclohexanol and *t*-butanol were dried by distillation on CaO, *N,N'*-dimethyl aniline and triethylamine by distillation on CaH<sub>2</sub>. Triethylene glycol monomethyl ether, cyclohexanone, 2,6-dimethyl-2-heptanol, (–)methyl-L-lactate, (–)ethyl-L-lactate, menthol, 1,1,1,3,3,3-hexafluoro-2-propanol, cyclooctanol, 2-phenyl-2-propanol and ethyl-2-hydroxy isobutyrate were commercial products which were distilled prior to use or purified by column chromatography on Al<sub>2</sub>O<sub>3</sub>. Commercial 2,2'-azobisisobutyronitrile

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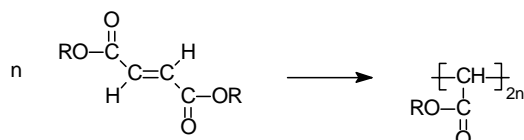


Fig. 1. Polymerization of di(alkyl fumarates) (DRFs).

(AIBN) and dimethyl 2,2'-azobisisobutyrate (MAIB) were recrystallized from ethanol, and potassium persulphate ( $K_2S_2O_8$ ) from water.

## 2.2. Monomers

Di(isopropyl) fumarate **1** and di(cyclohexyl) fumarate **2** were prepared by standard procedures [13].

Di(cyclooctyl) fumarate **3** was obtained analogously. The crude product was purified by flash chromatography (silica-gel, eluent: petroleum ether: ethyl acetate (8:2)). Yield: 90%, colourless viscous liquid.  $n_D^{20}$ : 1.5075.

Elemental analysis ( $C_{20}H_{32}O_4$ ).  $M_r = 336.38$ . Calculated: C = 71.39%, H = 9.59%. Found: C = 72.19%, H = 9.73%.  $^1H$ -NMR (200 MHz,  $CDCl_3$ ),  $\delta$  (ppm): 1.46–1.67 (m, 20H,  $CH_2$ ), 1.72–1.82 (m, 8H,  $CH_2$ ), 4.95–5.08 (m, 2H, O–CH), 6.77 (s, 2H, CH=CH).  $^{13}C$ -NMR (50 MHz,  $CDCl_3$ ),  $\delta$  (ppm): 22.7 ( $CH_2$ ), 25.2 ( $CH_2$ ), 27.0 ( $CH_2$ ), 31.2 ( $CH_2$ ), 76.1 (OCH), 133.9 (CH), 164.4 (C=O). IR (selected bands),  $\nu$  ( $cm^{-1}$ ): 2925 [alkyl CH], 1717 [C=O], 1646 and 981 [ $R^1HC=CHR^1$ (trans)], 1175 and 1114 [acyl–O–R].

Di(menthyl) fumarate **4** was obtained analogously. The crude product was purified by flash chromatography (silica-gel, eluent: petroleum ether: ethyl acetate (9.5:0.5)). Yield: 33%, colourless crystals, m.p.: 64°C.

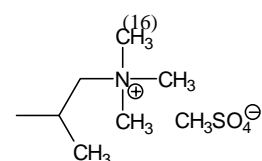
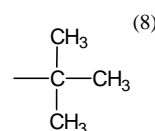
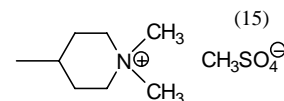
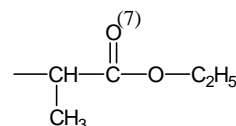
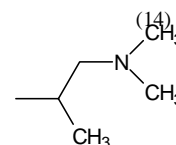
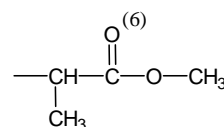
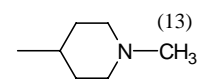
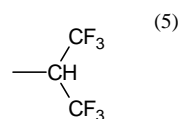
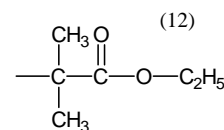
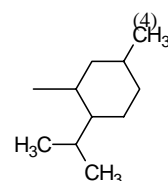
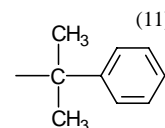
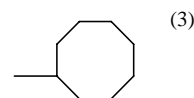
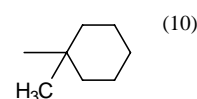
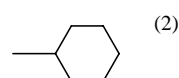
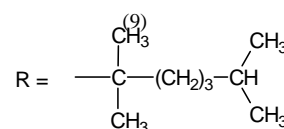
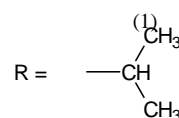
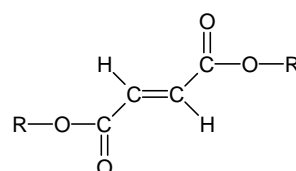
Elemental analysis ( $C_{24}H_{40}O_4$ ).  $M_r = 392.58$ . Calculated: C = 73.43%, H = 10.27%. Found: C = 73.61%, H = 10.51%.  $^1H$ -NMR (200 MHz,  $CDCl_3$ ),  $\delta$  (ppm): 0.75 (d, 6H,  $CH_3$ ), 0.88 (d, 6H,  $CH_3$ ), 0.92 (d, 6H,  $CH_3$ ), 1.00–1.72 (m, 14H,  $CH_2$ ), 1.86 (m, 2H, CH), 2.00 (m, 2H, CH), 4.78 (m, 2H, O–CH), 6.81 (s, 2H, CH=CH). The  $^{13}C$ -NMR spectrum agrees with the one reported in the literature [14]. IR, (selected bands),  $\nu$  ( $cm^{-1}$ ): 2957 and 2870 [CH alkyl], 1720 [C=O], 1650 and 978 [ $R^1HC=CHR^1$ (trans)], 1378; 1369 and 1462 [ $CH_3-C-CH_3$ ], 1214 and 1149 [acyl–O–R].

Di(hexafluoroisopropyl) fumarate **5** was obtained analogously. The crude product was purified by distillation in vacuo. Yield: 70%. Colourless crystals, m.p.: 56°C.

Elemental analysis ( $C_{10}H_4F_{12}O_4$ ).  $M_r = 416.12$ . Calculated: C = 28.86%, H = 0.97%. Found: C = 28.78%, H = 0.63%.  $^1H$ -NMR (200 MHz,  $CDCl_3$ ),  $\delta$  (ppm): 5.84 (m, 2H, O–CH), 7.12 (s, 2H, CH=CH).  $^{13}C$ -NMR (50 MHz,  $CDCl_3$ ),  $\delta$  (ppm): 67.4 (O–CH), 123.0 ( $CF_3$ ), 133.5 (CH=CH), 164.6 (C=O). IR, (selected bands),  $\nu$  ( $cm^{-1}$ ): 2977 [alkyl CH], 1733 [C=O], 1648 and 946 [ $R^1HC=CHR^1$ (trans)], 1200 [C–F], 1179 [acyl–O–R].

Di(methyl lactate) fumarate **6** was obtained analogously.

Table 1  
Studied fumarate monomers (DRFs)



It was purified by flash chromatography (silicagel, eluent: petroleum ether: ethyl acetate (7:3)). Yield: 56%, colourless viscous liquid.  $n_D^{20}$ : 1.4490.

Elemental analysis (C<sub>12</sub>H<sub>16</sub>O<sub>8</sub>).  $M_r$  = 288.25. Calculated: C = 50.00%, H = 5.59%. Found: C = 50.02%, H = 5.57%. <sup>1</sup>H-NMR (200 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 1.56 (d, 6H, CH<sub>3</sub>), 3.77 (s, 6H, CH<sub>3</sub>-O), 5.22 (q, 2H, CH-O), 6.97 (s, 2H, CH=CH). <sup>13</sup>C-NMR (50 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 16.7 (CH<sub>3</sub>), 52.2 (CH<sub>3</sub>-O), 69.2 (CH-O), 133.4 (CH=CH), 163.8 (C=O), 170.4 (C=O). IR, (selected bands),  $\nu$  (cm<sup>-1</sup>): 2997 and 2958 [alkyl CH], 1759 and 1729 [C=O], 1647 and 981 [R<sup>1</sup>HC=CHR<sup>1</sup>(trans)], 1217 and 1098 [acyl-O-R].

Di(ethyl lactate) fumarate **7** was obtained analogously. The crude product was purified by flash chromatography (silicagel, eluent: petroleum ether: ethyl acetate (7:3)). Yield: 77%, colourless viscous liquid.  $n_D^{20}$ : 1.4420.

Elemental analysis (C<sub>14</sub>H<sub>20</sub>O<sub>8</sub>).  $M_r$  = 316.31. Calculated: C = 53.16%, H = 6.37%. Found: C = 52.07%, H = 6.26%. <sup>1</sup>H-NMR (200 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 1.27 (t, 6H, CH<sub>3</sub>-CH<sub>2</sub>), 1.56 (d, 6H, CH<sub>3</sub>-CH), 4.23 (q, 4H, CH<sub>3</sub>-CH<sub>2</sub>), 5.19 (q, 2H, CH-O), 6.98 (s, 2H, CH=CH). <sup>13</sup>C-NMR (50 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 13.3 (CH<sub>3</sub>), 16.8 (CH<sub>3</sub>), 61.5 (CH<sub>2</sub>), 69.4 (CH-O), 133.6 (CH=CH), 164.0 (C=O), 170.1 (C=O). IR, (selected bands),  $\nu$  (cm<sup>-1</sup>): 2989 and 2944 [alkyl CH], 1755 and 1731 [C=O], 1648 and 979 [R<sup>1</sup>HC=CHR<sup>1</sup>(trans)], 1208 and 1096 [acyl-O-R].

Di(*t*-butyl) fumarate **8** was synthesized from fumaryl chloride with an equimolar mixture of *t*-butanol and methyl magnesium chloride [15].

Di(2,6-dimethyl hept-2-yl) fumarate **9** was obtained analogously. The crude product was purified by flash chromatography (silicagel, eluent: petroleum ether: ethyl acetate (9.75:0.25)). Yield: 48%, colourless viscous liquid.  $n_D^{20}$ : 1.4440.

Elemental analysis (C<sub>22</sub>H<sub>40</sub>O<sub>4</sub>).  $M_r$  = 368.56. Calculated: C = 71.70%, H = 10.94%. Found: C = 71.95%, H = 11.06%. <sup>1</sup>H-NMR (200 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 0.87 (d, 12H, CH<sub>3</sub>-CH), 1.22 (m, 4H, CH<sub>2</sub>-CH), 1.34 (m, 4H, CH<sub>2</sub>), 1.46 (s, 12H, C-CH<sub>3</sub>), 1.56 (m, 2H, CH), 1.77 (t, 4H, C-CH<sub>2</sub>), 6.67 (s, 2H, CH=CH). <sup>13</sup>C-NMR (50 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 21.6 (CH<sub>2</sub>), 22.6 (CH<sub>3</sub>), 26.0 (CH<sub>3</sub>), 27.8 (CH), 39.1 (CH<sub>2</sub>), 41.0 (CH<sub>2</sub>), 84.0 (C-O), 134.5 (vinyl CH), 164.3 (C=O). IR, (selected bands),  $\nu$  (cm<sup>-1</sup>): 2955 and 2871 [alkyl CH], 1716 [C=O], 1648 and 981 [R<sup>1</sup>HC=CHR<sup>1</sup>(trans)], 1469; 1386 and 1269 [CH<sub>3</sub>] 1210 and 1087 [acyl-O-R].

Di(1-methyl cyclohexyl) fumarate **10** was obtained analogously. The crude product was purified by flash chromatography (silicagel, eluent: petroleum ether: ethyl acetate (9.75:0.25)). Yield: 47%. Colourless crystals, m.p.: 54°C.

Elemental analysis (C<sub>18</sub>H<sub>28</sub>O<sub>4</sub>).  $M_r$  = 308.42. Calculated: C = 70.10%, H = 9.15%. Found: C = 70.09%, H = 9.08%. <sup>1</sup>H-NMR (200 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 1.36–1.51 (m, 20H, CH<sub>2</sub>), 2.09–2.16 (m, 6H, CH<sub>3</sub>), 6.65 (s, 2H,

CH=CH). <sup>13</sup>C-NMR (50 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 22.0 (CH<sub>2</sub>), 25.2 (CH<sub>2</sub>), 25.3 (CH<sub>3</sub>), 36.5 (CH<sub>2</sub>), 83.3 (CH), 134.5 (CH=CH), 164.3 (C=O). IR, (selected bands),  $\nu$  (cm<sup>-1</sup>): 2973 and 2933 [alkyl CH], 1711 [C=O], 1652 and 978 [R<sup>1</sup>HC=CHR<sup>1</sup>(trans)], 1450 and 1367 [CH<sub>3</sub>], 1254 and 1042 [acyl-O-R].

Di(1,1-dimethyl benzyl) fumarate **11** was obtained analogously. The crude product was recrystallized repeatedly from petroleum ether. Yield: 92%. Colourless crystals, m.p.: 65°C.

Elemental analysis (C<sub>22</sub>H<sub>24</sub>O<sub>4</sub>).  $M_r$  = 352.43. Calculated: C = 74.98%, H = 6.97%. Found: C = 74.85%, H = 6.81%. <sup>1</sup>H-NMR (200 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 1.71 (s, 12H, CH<sub>3</sub>), 6.67 (s, 2H, CH=CH), 7.15–7.25 (m, 10H, CH aryl). <sup>13</sup>C-NMR (50 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 28.5 (CH<sub>3</sub>), 83.0 (C-O), 124.3 (CH aryl), 127.2 (CH aryl), 128.4 (CH aryl), 134.5 (CH=CH), 145.1 (C aryl), 163.7 (C=O). IR, (selected bands),  $\nu$  (cm<sup>-1</sup>): 2984 and 2946 [alkyl CH], 1722 [C=O], 1665 and 979 [R<sup>1</sup>HC=CHR<sup>1</sup>(trans)], 1382 and 1365 [CH<sub>3</sub>], 1272 and 1075 [acyl-O-R].

Di(2,2'-dimethyl ethyl propionate) fumarate **12** was obtained analogously. The crude product was purified by flash chromatography (silicagel, eluent: ethyl acetate). Yield: 85%. Colourless crystals, m.p.: 56°C.

Elemental analysis (C<sub>16</sub>H<sub>24</sub>O<sub>8</sub>).  $M_r$  = 316.31. Calculated: C = 55.81%, H = 7.02%. Found: C = 55.78%, H = 7.08%. <sup>1</sup>H-NMR (200 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 1.21 (t, 6H, CH<sub>3</sub>-CH<sub>2</sub>), 1.57 (s, 6H, CH<sub>3</sub>-C), 4.15 (q, 4H, CH<sub>3</sub>-CH<sub>2</sub>), 6.82 (s, 2H, CH=CH). <sup>13</sup>C-NMR (50 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 14.0 (CH<sub>3</sub>), 24.5 (CH<sub>3</sub>), 61.5 (CH<sub>2</sub>), 79.4 (C-O), 133.8 (CH=CH), 164.0 (C=O), 171.9 (C=O). IR, (selected bands),  $\nu$  (cm<sup>-1</sup>): 2991 and 2945 [alkyl CH], 1740 and 1713 [C=O], 1667 and 989 [R<sup>1</sup>HC=CHR<sup>1</sup>(trans)], 1473 and 1385 [CH<sub>3</sub>], 1208 and 1096 [acyl-O-R].

Di(*N*-methylpiperid-4-yl) fumarate **13**:

7.2 g (0.062 mol) of 4-hydroxy-*N*-methyl-piperidine are added to a suspension of 7.2 g (0.068 mol) of powdered anhydrous Na<sub>2</sub>CO<sub>3</sub> in 50 ml of CH<sub>2</sub>Cl<sub>2</sub>. While cooling and stirring, 5.0 g (0.033 mol) of fumaryl chloride in 15 ml of CH<sub>2</sub>Cl<sub>2</sub> are added dropwise. The mixture is stirred for 4 h at room temperature. The precipitate is removed by filtration, the filtrate washed three times with half-saturated aqueous Na<sub>2</sub>CO<sub>3</sub>, passed over neutral Al<sub>2</sub>O<sub>3</sub> and evaporated. The crude product is recrystallized from diethyl ether. Yield: 2.5 g (25%). Colourless crystals, m.p.: 114°C.

Elemental analysis (C<sub>16</sub>H<sub>26</sub> N<sub>2</sub>O<sub>4</sub>S<sub>2</sub>).  $M_r$  = 310.44. Calculated: C = 61.90%, H = 8.46%, N = 9.02%. Found: C = 61.63%, H = 7.67%, N = 8.88%. <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>),  $\delta$ (ppm): 1.75, 1.9 (m, 4H + 4H, CH<sub>2</sub>-C-OOC), 2.1–2.3, 2.65 (m, 10H + 4H, CH<sub>2</sub>-N, CH<sub>3</sub>-N), 4.85 (m, 2H, CH-OOC), 6.8 (s, 2H, CH=CH).

Di(*N,N*-dimethylaminoprop-2-yl) fumarate **14** is prepared as diastereoisomeric mixture from racemic dimethylamino-2-propanol and fumaryl chloride in analogy to the fumarate **13**, as described above, in 50% yield. After evaporation of the solvent, the crude product is purified by

Table 2  
Homopolymerization of simple alkyl and cycloalkyl fumarates in bulk

DRF	AIBN (mol% of monomer)	T (°C)	Time (h)	Yield (%)	$M_n \times 10^{-4a}$	$M_w \times 10^{-4a}$	$M_w/M_n^a$
<b>1</b>	2.1	60	24	73	5.2	8.3	1.6
	2.4	75	24	53	3.7	5.6	1.5
<b>2</b>	2.0	60	24	26	1.7	3.2	1.9
	2.5	65	24	35	1.6	3.2	2.0
<b>3</b>	2.0	75	16	22	4.3	10.3	2.4
	1.5	65	24	12	0.37	0.49	1.3
<b>4</b>	2.1	65	24	15	0.33	0.45	1.4
	2.3	65	24	7	0.40	0.48	1.2
<b>8</b>	1.5	75	24	69	2.0	4.8	2.4
	2.0	75	16	55	5.6	10.1	1.8
<b>9</b>	2.0	75	24	70	2.3	5.8	2.5
	7.3	75	16	60	–	–	–
	1.0	65	18	6	0.4	1.3	3.2
<b>10</b>	1.0	65	24	3	0.7	1.2	1.7
	1.0	65	20	14	1.0	1.8	1.8
	1.7	65	24	12	0.9	1.4	1.6

<sup>a</sup> By SEC in THF, using polystyrene standards.

distillation in vacuo; b.p.<sub>0.2mmHg</sub>: 105°C. Yield: 8.89 g (48%). Slightly yellow liquid.

<sup>1</sup>H-NMR (200 MHz, CDCl<sub>3</sub>),  $\delta$ (ppm): 1.15 (d, 6H, CH<sub>3</sub>–C–OOC); 2.05–2.50 (m, 16H, CH<sub>2</sub>–N, CH<sub>3</sub>–N), 5.0 (m, 2H, CH–OOC), 6.7 (s, 2H, CH=CH).

Di(*N,N*-dimethyl piperidinio-4-yl) fumarate methylsulphate **15**:

Two grams ( $6.3 \times 10^{-3}$  mol) of diester **13** are dissolved

in 40 ml of hot acetonitrile. 1.5 ml of dimethyl sulphate are added and the mixture is stirred for 4 h at room temperature. The solution is filtered and the solid is washed with acetonitrile and with diethyl ether. The crude product is recrystallized from a methanol/ethanol 1:2 mixture. Yield: 59%. Colourless solid, m.p. 184°C.

Elemental analysis (C<sub>20</sub>H<sub>38</sub>N<sub>2</sub>O<sub>12</sub>S<sub>2</sub>).  $M_r = 562.74$ . Calculated: C = 42.68%, H = 6.82%, N = 4.98%, S =

Table 3  
Homopolymerization of functionalized fumarates in bulk, or in concentrated solutions

DRF	initiator (mol% of monomer)	T (°C)	Time (h)	Yield (%)	$M_n \times 10^{-4a}$	$M_w \times 10^{-4a}$	$M_w/M_n^a$
<b>5</b>	0.9 <sup>b</sup>	60	120	0	–	–	–
	0.9 <sup>c</sup>	60	24	0	–	–	–
	5.0 <sup>c</sup>	60	24	0	–	–	–
<b>6</b>	1.9 <sup>b</sup>	65	24	0	–	–	–
	1.3 <sup>c</sup>	65	24	19	1.5	2.0	1.3
<b>7</b>	1.9 <sup>c</sup>	65	24	34	2.3	3.3	1.4
	1.8 <sup>b</sup>	65	24	0	–	–	–
	1.3 <sup>c</sup>	65	24	Trace	–	–	–
<b>11</b>	1.4 <sup>c</sup>	65	24	Trace	–	–	–
	2.0 <sup>b</sup>	65	24	Trace	–	–	–
	1.4 <sup>c,d</sup>	65	48	0	–	–	–
<b>12</b>	1.8 <sup>c</sup>	65	24	16	–	–	–
	2.1 <sup>c</sup>	65	24	Trace	–	–	–
	1.2 <sup>b</sup>	65	24	0	–	–	–
<b>13<sup>e</sup></b>	2.3 <sup>b</sup>	65	24	Trace	–	–	–
	2.0 <sup>b</sup>	80	48	0	–	–	–
<b>14</b>	2.0 <sup>b</sup>	75	18	Trace	–	–	–
<b>15<sup>f</sup></b>	2.0 <sup>g</sup>	80	72	13	–	–	–
<b>16<sup>f</sup></b>	2.0 <sup>g</sup>	80	48	0	–	–	–

<sup>a</sup> By SEC in THF, using polystyrene standards.

<sup>b</sup> Initiator: AIBN.

<sup>c</sup> Initiator: MAIB.

<sup>d</sup> In the presence of 5% mol of 2,6-di-*t*-butyl pyridine.

<sup>e</sup> 56% by weight in *N,N*-dimethyl acetamide.

<sup>f</sup> 66% by weight in water.

<sup>g</sup> Initiator: K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>.

11.39%. Found: C = 42.66%, H = 6.11%, N = 4.81%, S = 11.99%.  $^1\text{H-NMR}$  (200 MHz,  $\text{D}_2\text{O}$ ),  $\delta(\text{ppm})$ : 1.8–2.25 (m, 8H,  $\text{CH}_2\text{-C-OOC}$ ), 3.0 (m, 12H,  $\text{CH}_3\text{-N}^+$ ), 3.15–3.60 (m, 8H,  $\text{CH}_2\text{-N}^+$ ), 3.5 (s, 6H,  $\text{CH}_3\text{-O-SO}_3$ ), 5.0 (m, 2H,  $\text{CH-OOC}$ ), 6.75 (s, 2H,  $\text{CH=CH}$ ).

Di(*N,N,N*-trimethylammonio-prop-2-yl) fumarate methylsulphate **16** (diastereoisomeric mixture) is prepared from **14** and dimethylsulphate in analogy to the piperidinium salt **15**, as described above, in 57% yield. The crude product is recrystallized from ethanol. Colourless powder, m.p.: 204°C.

Elemental analysis ( $\text{C}_{18}\text{H}_{38}\text{N}_2\text{O}_{12}\text{S}_2$ ).  $M_r = 538.72$ . Calculated: C = 40.13%, H = 7.12%, N = 5.20%, S = 11.91%. Found: C = 39.96%, H = 7.03%, N = 5.35%, S = 12.26%.  $^1\text{H-NMR}$  (200 MHz,  $\text{D}_2\text{O}$ ),  $\delta(\text{in ppm})$ : 1.2 (d, 6H,  $\text{CH}_3\text{-C-OOC}$ ), 3.0 (s, 18H,  $\text{CH}_3\text{-N}^+$ ), 3.5 (s, 6H,  $\text{CH}_3\text{-O-SO}_3$ ), 3.3–3.75 (m, 4H,  $\text{CH}_2\text{-N}^+$ ), 5.35 (m, 2H,  $\text{CH-OOC}$ ), 6.75 (s, 2H,  $\text{CH=CH}$ ).

### 2.3. Polymerization procedure

Polymerization was carried out in bulk in a sealed glass tube at different temperatures (60–80°C). 0.9–7.0 mol% of initiator (AIBN, MAIB or  $\text{K}_2\text{S}_2\text{O}_8$ ) was added to about 0.5 g of monomer. The vessels were degassed by three freezing-gas pumping–heating cycles followed by addition of argon. Polymerization conditions are given in Tables 2 and 3. After polymerization for the given time, the contents of the tube were precipitated twice into a large amount of methanol to recover the polymers. Only in the cases of **13**, **15** and **16**, concentrated solutions of monomers were reacted, as the melting points were too high, to allow polymerization below 100°C.

### 2.4. Measurements

$^1\text{H-NMR}$ ,  $^{13}\text{C-NMR}$  spectra were recorded on Gemini 200 and VXR 200 spectrometers in  $\text{CDCl}_3$  or in  $\text{D}_2\text{O}$ . Thermogravimetry was performed on a Setaram model TGC85 under nitrogen, applying a heating rate of 10°C/min. Differential scanning calorimetry was performed with a Perkin–Elmer DSC7, applying a heating rate of 10°C/min. X-ray powder diffractograms were obtained on a diffractometer D-500 (Siemens), using the Ni-filtered  $\text{CuK}\alpha$ -line ( $\lambda = 0.1541 \text{ nm}$ ). The molar mass of the samples was estimated by size exclusion chromatography (SEC) at 30°C in THF as eluent with standard polystyrenes (Tosoh). SEC was performed with a Tosoh 8000 series SEC systems equipped with TSK-gel columns 66000 HXL, G4000HXL2 and G2000HX. IR spectra were taken on FT-IR Nicolet 205 and FT-IR Perkin–Elmer 1710 spectrometers. Microanalysis was performed by the University College London.

## 3. Results and discussion

### 3.1. Monomers used

Whereas di(methyl) fumarate and di(ethyl) fumarate lead to oligomers only, fumarates with bulky substituents such as di(isopropyl) fumarate **1**, di(cyclohexyl) fumarate **2**, and in particular di(*t*-butyl) fumarate **8** were shown to homopolymerize [2]. The increase in polymerization reactivity of the fumarates by incorporating bulky groups was shown to result from the extremely slow bimolecular termination of the substituted polymethylene radicals with a rigid chain structure, thus overcompensating the slowing down of the propagation step [2,16]. But so far it is not clear, what is the optimal crowding of the substituents to promote polymerization, i.e. without interfering with the propagation step too much, as e.g. adamantyl fumarates are known not to polymerize well [17].

In order to establish the effects of alkyl substitution of the cyclohexyl ring and of ring size on polymerizability, we synthesized the fumarates bearing cyclooctyl **3**, menthyl **4** and 1-methyl cyclohexyl **10**. In addition, we synthesized di(2,6-dimethyl heptyl) fumarate **9** to study the influence of the branching of the alkyl chain on polymerization. The fumarate monomers studied are listed in Table 1.

We have also explored the introduction of functional groups into the fumarate monomers. This problem is non-trivial, as the propagation reaction of sterically crowded fumarates is strongly slowed down [2,16]. This implies that the polymerization is extremely sensitive to normally negligible side reactions, which may derive from the presence of functional groups, leading to potentially weak points to free radical attack. Such reactions may be normally too slow to influence the polymerization; however, for DRFs they may become decisive and may interfere with the polymerization. In fact, DRFs require much more painstaking purification than standard monomers, such as styrene or acrylics, to allow free radical polymerization, and the strict absence of even traces of oxygen.

We prepared first di(hexafluoroisopropyl) fumarate **5** and di(1,1-dimethyl benzyl) fumarate **11** which do not contain obvious sites prone to radical attack. Also, functionalized fumarates monomers bearing additional ester groups (**6**, **7** and **12**) were made. The  $\alpha$ -position of the esters is potentially a weak site [18]. Further, functionalized fumarate monomers with amino groups (**13** and **14**) were prepared in order to prepare polyelectrolytes. The  $\alpha$ -methyl and methylene groups of the amine moiety are known to be even more susceptible to radical attack [18]. This problem may be overcome by quaternization, which should result in strong polycations upon polymerization of fumarates **15** and **16** with a very high density of ionic groups. Such charged substituents might further enhance the increased rigidity of such polymers, and lead to a new class of sterically rigidified polyelectrolytes.

The structure of monomers **15** and **16** resembles some

reactive cationic surfactants [19]. Surface tension measurements showed that they exhibit a low surface activity only, lowering the surface tension of aqueous solutions at high concentrations (surface tension of solutions of 100g/l: 50 mN/m for **15**, and 54 mN/m for **16**). Thus the hydrophobic moieties are too short compared to the hydrophilic groups, and micellar association in water which might help the polymerization [20] can be excluded.

### 3.2. Homopolymerization of the fumarates (DRFs)

The results of radical polymerization of various DRFs with AIBN, MAIB or  $K_2S_2O_8$  in bulk or in solution at different temperatures (60–80°C) are summarized in Tables 2 and 3. Clearly, the average molar masses ( $M_n$  and  $M_w$ ), polydispersities and yields depend sensitively on the structure of the ester substituents.

Concerning the simple alkyl and cycloalkyl DRFs **1–4**, and **8–10** (Table 2), the best results were obtained with **8**, i.e. with the simple *t*-butyl group substituent, followed by the isopropyl ester **1** and by the cyclohexyl ester **2**. The tertiary ester di(2,6-dimethyl hept-2-yl) fumarate **9** gives rather low yields, and lower estimated molar masses. As even very long alkyl chains of tertiary esters have been shown to be not particularly disadvantageous for the polymerization of DRFs [15], the reduced polymerizability compared to **8** might be related to the presence of the methyl branch, i.e. of a methine group, which is more vulnerable to radical attack than simple methylene or methyl groups [18,21]. Within this line, the limited polymerizability of the menthyl ester **4** may derive from the presence of two methine groups. The substitution of the cyclohexyl ring in the 2-position presumably plays a role too, due to too much of steric crowding as proposed before [14]. The same argument holds true for the limited polymerizability of the cyclooctyl ester **3**. The idea of an optimum steric crowding to promote polymerizability is supported by the intermediate polymerizability of the 1-methyl cyclohexyl ester **10**. Therefore, to explore the possibility of functionalization, we have concentrated on unbranched derivatives of the isopropyl, the *t*-butyl and the cyclohexyl residues, which are functionalized at their outermost position.

The tertiary benzyl ester **11** is polymerizable, so that replacing a methyl by a phenyl group in comparison to **8** does not result in a too bulky structure. However, the polymer obtained from **11** is insoluble. In fact, the tertiary benzyl ester moiety proved to be unstable under the polymerization conditions, leading to partial decomposition of the ester during polymerization itself: in the I.R. spectrum, the ester carbonyl band of poly(DRF)s, typically located around 1705–1730  $cm^{-1}$ , is replaced by a new large band centered at 1685  $cm^{-1}$ , which points to conversion to –COOH groups. Presumably, the ester is mainly eliminated as  $\alpha$ -methylstyrene, whose conjugation facilitates the cleavage. We hypothesized that traces of acid present would catalyze the ester cleavage. Therefore the polymerization

was attempted in the presence of an acid scavenger such as 2,6-di-*t*-butyl pyridine; however, no polymer could be obtained under these conditions. Therefore, the use of benzyl derivatives seems to present no useful alternative for the design of fumarate monomers.

In spite of the optimized monomer architecture, all functionalized monomers **6–7**, and **12–16** (Table 3) exhibit very low polymerizability. Numerous attempts at polymerization performed under different conditions (temperature, small amounts of solvent...) failed when using the initiator AIBN. This result is hardly surprising for **13** and **14**, since  $\alpha$ -CH fragments of amines are known to be somewhat sensitive to radical side reactions [18]. This problem is aggravated in the case of **13** by the high melting point which precludes from bulk polymerization. It imposes the use of a solvent, which—despite of the high monomer concentration—renders the polymerization of DRFs more difficult [2,16]. The difficulties in polymerizing the lactate esters **6** and **7** are stronger evidence for the problematic polymerization of DRFs, as ester fragments are usually supposed to be nearly inert in free radical polymerization [18]. Obviously, the particularity of the DRF polymerization, i.e. the strong decrease of the propagation rate constant, is a major obstacle to exploiting the easily accessible, densely functionalized fumarates for the making of more complex homopolymers.

Nevertheless, when using MAIB instead of AIBN, polymers are obtained from fumarates **6**, **7** and **12**, though in low yield. So the functionalization of DRF monomers by an additional ester group seems to be just tolerable for polymerization. Otsu et al. have found, too, that the polymerizability of DRFs depends significantly on the initiator chosen [22–24], MAIB giving better results than AIBN. A more detailed investigation of initiator effects is forthcoming [25].

Due to the high melting points of the ammonium salts **15** and **16**, the cationic monomers had to be polymerized in concentrated aqueous solutions (Table 3). The success of the polymerization of monomer **15**, initiated by  $K_2S_2O_8$ , is interesting although yields are low. It is not clear whether a high molar mass polymer is obtained, or rather, an oligomer. Attempts to estimate the molar masses by SEC failed, due to absorption onto the column material. The shape of the  $^1H$ -NMR spectra supports rather the first view, due to the width of the signals, and the lack of any signal which could be attributed to end groups. In any case, the failure of polymerizing the analog **16** demonstrates once more that we deal with a limiting case. Nevertheless it should be underlined that these difficulties are only characteristic for the homopolymerization of DRFs. Copolymerization with electron rich comonomers such as styrene or vinylacetate, however, should proceed easily, as shown before [26–28].

The steric crowding of the trifluoromethyl groups should render **5** comparable to **8**, and the  $\alpha$ -CF<sub>3</sub> groups should even stabilize the CH group of the secondary ester against radical attack [18]. So monomer **5** was expected to polymerize

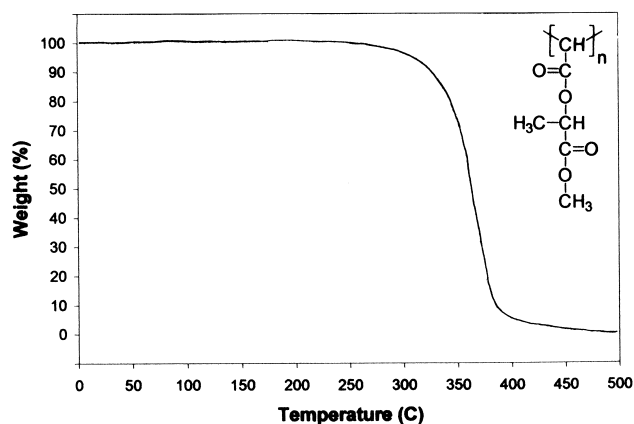


Fig. 2. Thermogram of poly(dimethyl lactate fumarate) **6**.

better than its hydrocarbon analog **1**, which however is not true: all attempts at polymerization of monomer **5** failed. We have no satisfactory explanation so far for the lacking polymerizability. The rather high wave number of  $1733\text{ cm}^{-1}$  of the carbonyl band in **5** compared to  $1718\text{ cm}^{-1}$  in **1** might indicate either a less efficient conjugation of the ester groups with the double bond, or a higher deficiency in electron density; both effects might reduce the homopolymerizability. Alternatively, we may speculate that the fluorocarbon groups shield the double bond efficiently against diffusing hydrocarbon radicals deriving from AIBN or from MAIB.

### 3.3. Characterization of the poly(fumarates) (poly(DRFs))

All poly(DRF)s are colourless powders that are soluble in solvents such as benzene, toluene, THF or chloroform, but are insoluble in methanol.

The  $^1\text{H-NMR}$  spectra show the loss of the signals at 6.9 ppm characteristic for the protons of the double bond in the monomers, and exhibit a new large signal at about 3 ppm attributed to the methine proton of the backbone. Also, the  $^{13}\text{C-NMR}$  spectra show the loss of the signal around 130 ppm of the ethylenic carbons, while a new

signal at 45–50 ppm appears, attributed to the methine group of the backbone. The chemical shift of the other signals is hardly changed upon polymerization; however, the signals become strongly broadened. In parallel in the IR spectra of poly(DRF)s, the carbonyl peak of the ester bond which is located at about  $1720\text{ cm}^{-1}$  for the monomers, is shifted to higher wave numbers of about  $1730\text{ cm}^{-1}$  upon polymerization.

The thermal stability of poly(DRF)s was investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Typical thermograms are exemplified by poly-**6** and by poly-**10** in Figs. 2 and 3. Decomposition temperatures are summarized in Table 4. The thermogravimetric analysis exhibited thermal stability up to  $200^\circ\text{C}$  for polymers containing tertiary esters and up to  $250^\circ\text{C}$  for the other polymers (Table 4). The thermograms in Figs. 2 and 3 show that the degradation of poly(DRF)s shows one big step if the DRF has a secondary ester group (Fig. 2), but two distinguishable big steps if the DRF has a tertiary ester (Fig. 3). The first degradation step is attributed to the cleavage of the ester bond at around  $200^\circ\text{C}$  and the elimination of the resulting olefin [1,2]. The second degradation step is attributed to the degradation of the main chain occurring at around  $250\text{--}300^\circ\text{C}$ .

Differential scanning calorimetry (DSC) showed that poly(fumarates) typically do not show a glass transition temperature ( $T_g$ ) below their degradation temperature [2,15]. This observation is also true for most of the polymers prepared in this work. Exceptionally thermal transitions were found for poly(diisopropyl fumarate) **1**,  $T_g$  of  $74^\circ\text{C}$ ; for poly(dimethyl lactate fumarate) **6**,  $T_g$  of  $66^\circ\text{C}$  and for poly(di-2,6-dimethyl heptyl fumarate) **9**,  $T_g$  of  $-3^\circ\text{C}$ . The particularly low  $T_g$  found for poly(di-2,6-dimethyl heptyl fumarate) **9** can be rationalized by an intramolecular plasticizing effect of the branched substituents.

Wide-angle X-ray diffraction (WAXD) of selected polymers demonstrates the occurrence of suprastructures in the poly(DRF)s (Fig. 4). In addition to a diffuse halo centred at angles of about  $20^\circ$  for  $2\theta$ , an additional scattering maximum is observed at scattering angles of about  $7\text{--}8^\circ$ . This additional signal is particularly pronounced for compact ester substituents as found in polymers of **1** and **8**, but it is also present for all other poly(DRF)s which were studied. The d-spacings calculated from the scattering peaks according to the Bragg equation are listed in Table 5. The smaller spacing  $d_2$  of 0.45 to 0.50 nm calculated from the position of the halos is common to all poly(DRF)s, and may be associated with the repeat unit of the rigid polymer backbone [15,29,30]. The larger spacing,  $d_1$ , corresponding to the broad peak observed at angles  $2\theta$  of about  $7\text{--}8^\circ$ , which increases with the size of the substituents, may correspond to the spacing between the polymer chains. The d-spacing of 1.15 nm for poly(di-*t*-butyl fumarate) **8** agrees well with the ones reported previously [15,29,30]. Also, the  $d_1$ -values of 1.23 and 1.25 nm for poly(dimethyl fumarate) **4** and for poly(di-1-methyl cyclohexyl fumarate) **10**, respectively, fit

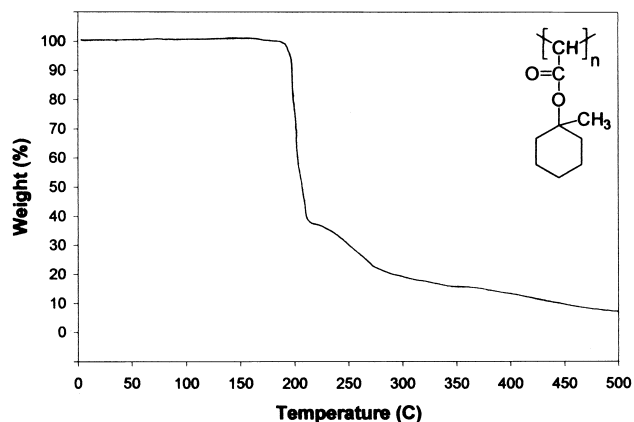


Fig. 3. Thermogram of poly(di-1-methyl cyclohexyl fumarate) **10**.

Table 4  
Decomposition temperatures for poly(DRF)s according to TGA

Polymer of DRF	Onset of first decomposition step (°C)	Onset of second decomposition step (°C)
1		260–270
2		290–295
3		245–250
4		260–265
6		265–275
8	195–200	295–300
9	200–205	250–255
10	210–215	255–260
11	120–130	255–260
12	255–260	(365–370)

Table 5  
Bragg spacings of poly(DRF)s

Polymer of DRF	Bragg spacing (nm)	
	$d_1$	$d_2$
1	1.05	0.45
4	1.23	0.50
6	1.18	0.42
8	1.15	0.48
10	1.25	0.52

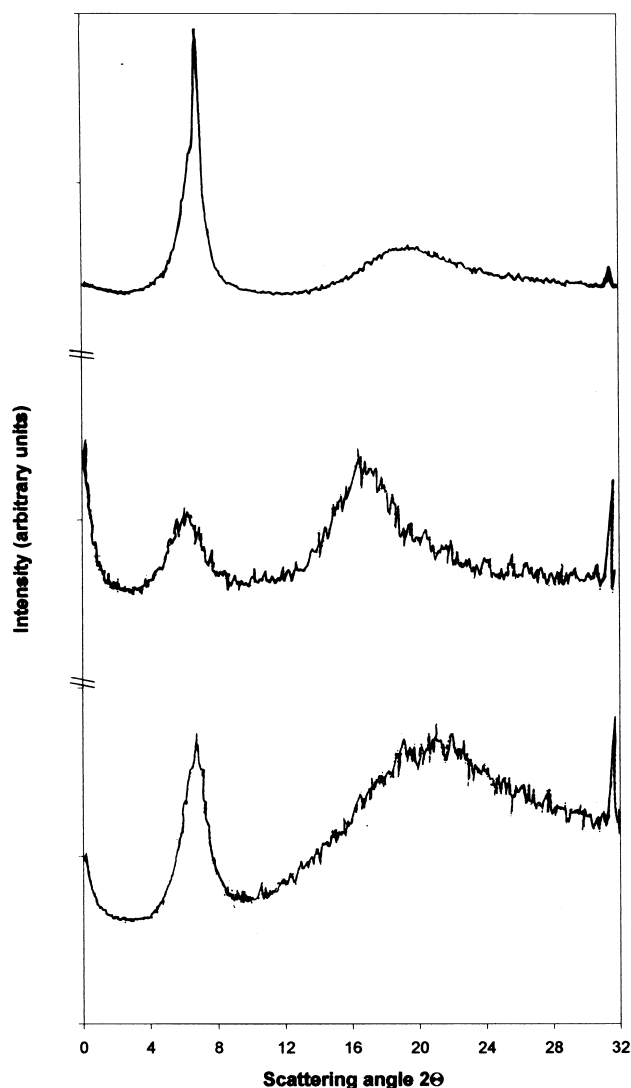


Fig. 4. WAXD powder diffractograms of poly(DRF)s. Top to bottom: poly(diisopropyl fumarate) **1**, poly(dimethyl fumarate) **4**, poly(di-1-methyl cyclohexyl fumarate) **10**.

well into the  $d_1$ -value of 1.28 nm reported in the literature [15,30] for poly(dicyclohexyl fumarate) **2**. The  $d_1$ -spacings are somewhat bigger for cyclic substituents. The organized arrangement of the polymers evidenced by the powder diffractograms while typical fragments inducing structuring at the molecular level, such as amphiphiles, mesogens, or long linear alkyl chains are absent, suggests that the poly(fumarates) have a rigidified polymer backbone, and may be considered as another example of “hairy rod” polymers [31]. Heating experiments in the optical microscope between cross-polarizers, however, did not give any indication for the occurrence of thermotropic crystalline phases, in agreement with the DSC experiments.

#### 4. Conclusions

We have prepared a variety of dialkyl fumarates (DRFs) bearing different substituents, in particular, by varying of ring size and substituents on the ring. Moreover, we have explored the possibility of the introduction of functional groups. The homopolymerization of dialkyl fumarates is very delicate. It is very sensitive to the structure of ester groups but also to the polymerization conditions (purity of monomers and initiators, presence of solvent and traces of oxygen). The *t*-butyl ester group seems to be rather optimal. The introduction of functional groups in the fumarates does not prevent automatically their polymerization, but it renders polymerization very difficult. When the initiator is properly chosen, at least one additional ester group is tolerated. A more detailed investigation of initiator effects is forthcoming. The presence of high glass transition temperatures beyond the thermal decomposition for the majority of poly(fumarates) suggests a rigidified backbone, which can be attributed to steric crowding. In agreement, X-ray diffraction shows the existence of suprastructures in the poly(DRF)s, but thermotropic mesophases were not observed.

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