Radical High Polymerization of Fumaric Acid Derivatives with Bulky Substituents: Synthesis of Poly(*N*,*N*,*N*′,*N*′-tetra-alkylfumaramide)s and Poly(alkyl *N*,*N*-diethylfumaramate)s

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Some *N*,*N*,*N*′,*N*′-tetra-alkylfumaramides and alkyl *N*,*N*-diethylfumaramates polymerize through an opening of their double bond with a radical initiator, in a similar way to dialkyl fumarates, leading to high molecular weight and semi- or non-flexible polymers consisting of a substituted polymethylene structure.

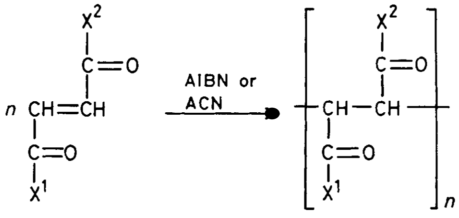
In general, 1,2-di-, tri-, and tetra-substituted ethylenes do not polymerize to give high molecular weight homopolymers with radical initiators, owing to the increased steric effect of the substituents. However, there are some exceptions, *i.e.* perfluoroethylenes like tetrafluoroethylene[1] and chlorotrifluoroethylene,[2] vinylene carbonate,[3,4] and *N*-substituted maleimides[5—8] *etc.*, which have been reported to homopolymerize easily.

These facts suggested that we re-examine systematically the homopolymerization behaviour of 1,2-disubstituted ethylenes, and we found that dialkyl fumarates[9—11] (**1a**) and methyl alkyl fumarates[12,13] (**1b**) homopolymerized with a radical initiator to yield high molecular weight and semi- or non-flexible poly(alkoxycarbonylmethylene) (**2a**). The polymerization reactivities (yield and molecular weight of the resulting polymer) of (**1a**) and (**1b**) increased with increase in

Table 1. Results of radical polymerization of (**1c**) and (**1d**).[a]

	Compound used							
	X^1	X^2	Temp. /°C	Time /h	Yield /%	[η] /dl g^{-1}	$\bar{M}_n \times 10^{-3}$ [b]	$\bar{M}_w/\bar{M}_n$ [b]
(**1c**)	NEt_2	NEt_2	80	10[c]	30.4	0.15	12	1.7
(**1c**)	NPr^i_2	NPr^i_2	80	12[c]	25.3	0.13	15	1.8
(**1d**)	OMe	NEt_2	80	50[d]	10.3	0.09	11[e]	1.3
(**1d**)	OPr^i	NEt_2	80	30[d]	12.8	0.06	7[f]	1.3
(**1a**)	OPr^i	OPr^i	60	10	29.1	0.85	110	2.0
(**1a**)	OBu^t	OBu^t	80	6	84.6	0.63	—	—
(**1b**)	OMe	OBu^t	60	10	23.5	0.45	—	—

[a] Polymerized in the presence of AIBN (20 mmol/l) in bulk. [b] The number- and weight-average molecular weights ($\bar{M}_n$ and $\bar{M}_w$, respectively) determined in tetrahydrofuran by gel permeation chromatography. [c] The monomer (5 mmol) was polymerized in the presence of ACN (0.05 mmol) in benzene (5 ml). [d] Polymerized in the presence of ACN (20 mmol/l) in bulk. [e] This polymer has $\bar{M}_n$ of 23 000 which was measured by membrane osmometry. [f] This polymer has $\bar{M}_n$ of 13 000.



(**1**) (**2**)

a; $X^1 = X^2 = OR$
b; $X^1 = OR$, $X^2 = OR'$
c; $X^1 = X^2 = NR_2$
d; $X^1 = OR$, $X^2 = NR_2$

the bulk of their ester alkyl substituents, *i.e.* t-butyl>s-butyl >iso-butyl≃n-butyl, in spite of an increase in their steric effect. Because the polymer chain becomes more rigid with a bulky substituent, it seemed that bimolecular termination of such a rigid propagating radical was occurring less, relative to its propagation reaction, thus giving higher molecular weights and faster polymerization rates.

To extend such results to fumaramide and fumaramate derivatives, we attempted to homopolymerize some of these compounds in the presence of 2,2′-azobisisobutyronitrile (AIBN) or 2,2′-azobiscyclohexanecarbonitrile (ACN). In a series of fumaramide derivatives, *N,N,N′,N′*-tetrasubstituted fumaramides were found to homopolymerize to give high molecular weight polymers, although fumaramide and its *N,N′*-disubstituted derivatives such as *N,N′*-diethylfumaramide did not undergo high polymerization which agreed with the results reported by Azuma *et al.*[14,15]

In this communication, we report the radical initiated high polymerization of *N,N,N′,N′*-tetrasubstituted fumaramides (**1c**) and alkyl *N,N*-diethylfumaramates (**1d**) (where R and R′ are alkyl groups), with AIBN or ACN as shown in Table 1, in which some results for (**1a**) and (**1b**)[13] are shown for comparison.

From Table 1, (**1c**) and (**1d**) are also observed to polymerize easily to give fairly high molecular weight homopolymers as observed with (**1a**) and (**1b**). The polymerization reactivities were approximately in the order: (**1a**)>(**1b**)>(**1c**)>(**1d**). In the series of (**1c**) and (**1d**), the order of polymerization reactivity by the substituents was $NEt_2 > NPr^n_2$ and $OPr^i >$ OMe (where X^2 is NEt_2), respectively. Since the bulkiness of NR_2 increases more than that of OR when the same R group was substituted, the difference in the order observed between (**1c**) and (**1d**) may be due to an increased bulkiness of the substituents.

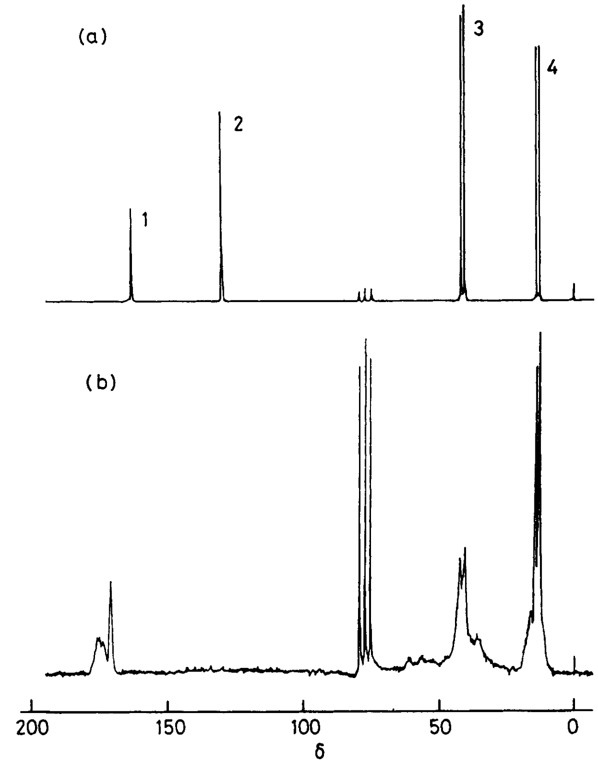


Figure 1. ^{13}C n.m.r. spectra of (a) *N,N,N′,N′*-tetraethylfumaramide and (b) the polymer in $CDCl_3$ with tetramethylsilane as an internal standard at room temperature: (1) carbonyl, (2) vinylene, (3) methylene, and (4) methyl carbons.

In a series of (**1c**), however, a reversed order with respect to the bulkiness is observed, contrary to (**1a**), (**1b**), and (**1d**). It may be that there is a limitation between the bulkiness of the substituents and the reactivity. If such bulkiness exceeds the maximum steric requirement in the transition state necessary to continue radical propagation, the polymerization may be retarded independent of the contribution of a lowered termination rate. In fact, *N,N,N′,N′*-tetraisopropylfumaramide was recently found to not polymerize.

Figure 1 shows the ^{13}C n.m.r. spectra of (**1c**) ($X^1 = X^2 = NEt_2$) and its polymer (**2c**). The absorption band at δ 130 due to the vinylene bond observed in the monomer disappeared from the spectra of the polymer, in which a new band at δ 50—60 due to a methine carbon appeared. Therefore, (**1c**) was found to polymerize by an opening of its double bond, *i.e.* an ordinary vinylene polymerization mechanism, to give poly-(*N*,*N*-dialkylaminocarbonylmethylene) (**2c**). A similar conclusion was also obtained for (**2d**), *i.e.* poly-(*N*,*N*-diethylaminocarbonylmethylene-*alt*-alkoxycarbonylmethylene) was produced from (**1d**).

The polymers, (**2c**) and (**2d**) were colourless powders and soluble in common organic solvents as were (**2a**) and (**2b**). The polymer (**2c**) ($X = X^2 = NEt_2$) was soluble in both benzene and water, and (**2d**) (X^1 = OMe or OPr^i, $X^2 = NEt_2$) was dissolved in both benzene and methanol. From the molecular model structures, it was concluded that (**2c**) and (**2d**) consist of semi- or non-flexible rodlike polymer chains, similar to (**2a**) and (**2b**).[10,11]

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