

Contribution to the study of the kinetics of radical homo- and copolymerization of fluoroalkyl methacrylates, 1

2-Chloro-2,3,3,3-tetrafluoropropyl methacrylate

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Introduction

As early as in the 1950's, Sandberg et al.¹⁾ studied the radical polymerization of acrylates and methacrylates containing perfluorinated alkyl chains of various lengths. Particular attention was paid to the polymerization and copolymerization of these monomers mainly because the products from the polymerization of these compounds show both thermal and chemical stability. Acrylates and methacrylates with longer perfluoroalkyl groups (C_n ; $n > 5$) and their saturated analogues may also be used for the synthesis of fluorinated telomers with surface-active properties²⁾, which predetermines them e.g. for the application in textile industry. In their paper³⁾, Narita et al. reported that fluorine-containing substituents might lead to a high electron-withdrawing effect lowering the electron density of the vinyl group and also the ability to polymerize through radical mechanism. The authors carried out a series of measurements. They compared Q - and e -values of fluoroalkyl acrylates and fluoroalkyl methacrylates with the Q , e -values of ethyl acrylate and ethyl methacrylate. Their assumption that these values are lower for monomers not containing fluorine in the side alkyl group than for acrylates and methacrylates containing fluorine was confirmed.

Narita et al.^{4–6)} also performed a series of experiments of anionic polymerization of 2,2,2-trifluoroethyl acrylate and methacrylate and 2,2,2-trifluoro-1-trifluoromethylethyl acrylate and methacrylate with various initiators of anionic polymerization to support the statement that the lowering of electron density of the vinyl group raises the ability of monomers to polymerize via anionic mechanism.

This paper reports on the experimental results of the determination of the initiation rate of radical polymerization of 2-chloro-2,3,3,3-tetrafluoropropyl methacrylate (FCPM) in benzene.

The rates of the polymerization of FCPM in solvents with various donor activities (benzene, acetonitrile, tetrahydrofuran, *N,N*-dimethylformamide) are compared. Copolymerization parameters for the pairs FCPM/methyl methacrylate, FCPM/butyl acrylate as well as Q , e -values for this monomer were determined.

Experimental part

Materials: 2-chloro-2,3,3,3-tetrafluoropropyl methacrylate (FCPM) was purified by vacuum distillation (b. p. 46,5–47,5 °C/2 kPa). Comonomers butyl acrylate (BA) (from Chemical Works, Sokolov), styrene (S) (from Kaučuk Kralupy) and methyl methacrylate (MMA) (from Chemical Works, Žilina) were purified by shaking with 10% aqueous NaOH solution, washing with distilled water and drying with CaCl_2 . The purified monomers were distilled under reduced pressure.

The solvents used [benzene, anal. grade (from Lachema, Brno), acetonitrile "purum" (from Laborchemie, Apolda, GDR), *N,N*-dimethyl formamide (from Laborchemie, Apolda, GDR)] were purified by distillation. Tetrahydrofuran, anal. grade (from Laborchemie, Apolda, GDR) was purified as usual⁷⁾. The initiator, 2,2'-azoisobutyronitrile (AIBN) "purum" (from Fluka AG, Switzerland), was recrystallized from methanol. The inhibitors (*p*-benzoquinone, as admixture to a precipitant of polymers and copolymers and 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl⁸⁾) were used without further precipitation.

Polymerizations: Homopolymerizations of FCPM and copolymerizations of FCPM with S and BA were carried out in benzene. The reaction mixture was introduced into a dilatometer where it was subjected to a three-fold freezing cycle under inert atmosphere and then to evacuation (freezing-thaw cycle). The dilatometer was then put into a water bath at $60 \pm 0,05$ °C. The concentration of the monomer or a mixture of monomers was in each case $2 \text{ mol} \cdot \text{dm}^{-3}$ of the system and the initiator concentration was $5 \cdot 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$.

Copolymerization of FCPM with MMA was carried out in bulk at an AIBN concentration of $6,7 \cdot 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$. Experiments were done to about 10% conversion. Homopolymers and copolymers were precipitated into methanol (anal. grade) containing a small amount of *p*-benzoquinone. The composition of the copolymers was determined from the data of elemental analysis; copolymerization parameters were calculated by the method of Kelen and Tüdös⁹⁾.

Results and discussion

The dependence of the inhibition period (t_{inh}) of the polymerization of FCPM in benzene on the concentration of the inhibitor, 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl (XH), was examined to find R_i for the given system and to determine the ratio of the rate constants according to the relation:

$$R_p = k_p/k_t^{0,5} (f \cdot k_d [\text{I}])^{0,5} \cdot [\text{M}] \quad (1)$$

where R_p is the rate of polymerization in $\text{mol} \cdot \text{dm}^{-3} \cdot \text{s}^{-1}$, k_p is the rate constant of propagation in $\text{dm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$; k_t is the rate constant of termination in $\text{dm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$, f is the efficiency of initiation, k_d is the rate constant of initiator decomposition in s^{-1} and [I] and [M] represent concentrations of initiator and monomer, respectively, in $\text{mol} \cdot \text{dm}^{-3}$.

Tab. 1 contains the experimental values of the reaction $t_{\text{inh}} = f([\text{XH}])$ for the particular system.

The slope of the linear dependence $\text{tg } \alpha = 1/R_i = 2,04 \cdot 10^7$, the rate of initiation $R_i = 4,9 \cdot 10^{-8} \text{ mol} \cdot \text{dm}^{-3} \cdot \text{s}^{-1}$ and the ratio of the rate constants $k_p/k_t^{0,5}$, calculated according to Eq. (1) using the values $R_p = 5,19 \cdot 10^{-5} \text{ mol} \cdot \text{dm}^{-3} \cdot \text{s}^{-1}$ and $R_i = 4,9 \cdot 10^{-8} \text{ mol} \cdot \text{dm}^{-3} \cdot \text{s}^{-1}$ is 0,165 (if¹⁰⁾ $f = 0,6$ and $k_d = 1,16 \cdot 10^{-5}$). For comparison, the ratio of the rate constants k_p/k_t for methyl methacrylate calculated according to ref.¹¹⁾ has the value 0,102.

Tab. 1. Dependence of the inhibition period (t_{inh}) on the concentration of inhibitor (XH) used

$[\text{XH}] \cdot 10^5$ ^{a)} $\text{mol} \cdot \text{dm}^{-3}$	$t_{\text{inh}}/\text{min}$
8,28	29
18,10	78
25,10	86

^{a)} [XH]: concentration of 4-hydroxy-2,2,6,6-tetramethylpyridine-1-oxyl.

During polymerization of FCPM in four different solvents (benzene, acetonitrile, tetrahydrofuran and *N,N*-dimethyl formamide), no significant effect of these solvents on the rates of polymerization was observed. Tab. 2 shows the measured values of the rates of polymerization in individual solvents as a function of the donor number¹²⁾ of the solvent used.

Tab. 2. Values of the rates of polymerization of FCPM in various solvents at 60 °C

Solvent	D_N ^{a)}	$R_p \cdot 10^5$ ^{b)} $\text{mol} \cdot \text{dm}^{-3} \cdot \text{s}^{-1}$
Benzene	0,1	5,19
Acetonitrile	14,1	5,13
Tetrahydrofuran	20,0	5,86
<i>N,N</i> -Dimethylformamide	26,6	6,57

^{a)} D_N : donor number.

^{b)} R_p : rate of polymerization.

As is seen from Tab. 2, the rate of polymerization slightly increases with increasing donor number of the solvent used, which may be connected with the levelling off of the electron density of the vinyl group under the solvent effect.

The copolymerization of FCPM with BA and with styrene was carried out in benzene, copolymerization of FCPM with MMA was performed in bulk.

The composition of the copolymers was determined from the results of the elemental analyses. The composition of individual copolymers is presented in Tab. 3: F_i = mol-% FCPM monomeric units in the copolymer dependent on the feed composition f_i = mol-% FCPM in the monomer mixture.

Tab. 4 contains the copolymerization parameters of individual monomer pairs calculated by the method of Kelen and Tüdös based on the composition of the copolymers.

The values of Q and e , determined for FCPM from the values of the copolymerization parameters of the FCPM/S pair and from the Q , e -values for styrene according

Tab. 3. Composition of copolymers of FCPM with BA, S and with MMA (F_i) as a function of the feed composition (f_i)

Comonomer	$f_i^a)$ in mol-%	$F_i^b)$ in mol-%
BA ^{c)}	80	58,7
	60	69,8
	50	48,0
	40	50,3
	20	35,3
S ^{c)}	80	66,4
	60	56,2
	50	49,7
	40	52,4
	20	40,6
MMA ^{d)}	76	73,6
	49	42,9
	40	43,7
	29	18,2
	8	8,2

a) f_i : feed composition (of monomer mixture).b) F_i : average copolymer composition.

c) Copolymerization carried out in solution (solvent: benzene).

d) Copolymerization in bulk.

Tab. 4. Copolymerization parameters of the pairs FCPM/BA, FCPM/S and FCPM/MMA

Comonomer M_2	r_1	r_2
BA ^{a)}	0,13	0,17
S ^{a)}	0,23	0,12
MMA ^{b)}	1,27	0,44

a) Copolymerization in solution.

b) Copolymerization in bulk.

to the authors¹³⁾, were $Q_{\text{FCPM}} = 1,79$ and $e_{\text{FCPM}} = 1,08$. These relatively high values indicate the electron-acceptor character of the side alkyl group of 2-chloro-2,3,3,3-tetrafluoropropyl methacrylate.

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