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Synthesis of telogens and optimization of tetrafluoroethene telomerization process

Grzegorz Lewandowski *, Egbert Meissner, Eugeniusz Milchert

Institute of Chemical Organic Technology, Szczecin University of Technology, PL-70-322 Szczecin, Půlaskiego 10, Poland

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Abstract

The most advantageous technological parameters of tetrafluoroethene telomerization using 1-chloro-2-iodohexafluoropropane (telogen) towards the telomers n2–n4 or n1–n4 were experimentally established. The telomers n1–n4 were prepared with the yield of 48 mol% under the following conditions: temperature 170 °C, the molar ratio of 1-chloro-2-iodohexafluoropropane to tetrafluoroethene equal to 1.2, the autoclave filling of 1.5 kg dm^{-3}. The maximum yield of telomers n2–n4 amounted to 27 mol% when the molar ratio of telogen to tetrafluoroethene was decreased to 0.7 and the other parameters of synthesis remained the same. The optimum parameters for the synthesis of telogens: 1-chloro-2-iodohexafluoropropane and 2-iodoheptafluoropropane have been also determined.

Keywords: Telomerization; Tetrafluoroethene; 1-Chloro-2-iodohexafluoropropane; 2-Iodoheptafluoropropane; Optimization

1. Introduction

Telomerization of tetrafluoroethene (TFE) is a particularly useful method for the preparation of many technically important compounds and intermediates. The addition of different amounts of TFE (taxogen) to telogen (*XY*) proceeds in accordance with the reaction (Scheme 1).

Typical initiators of polymerization include peroxides, percarbonates, 2,2′-azobis(isobutyronitrile) (AIBN) (radical initiation) as well as light (photochemical initiation) and elevated temperature (thermal initiation) methods. In the telogen molecule *X* is most often perfluoroalkyl, chloroperfluoroalkyl, perfluoroalkenyl, and perfluorocycloalkyl. *Y* denotes iodine or bromine.

A method of synthesis of such telogens [1–4] relies on the reaction of a perfluoroalkene with iodine and iodine(V) fluoride in the presence of catalysts, for example metallic aluminium, aluminium iodine, aluminium bromide [5], SbF_5, SbF_3, ZnF_2 [6], and $TiCl_4$, $ZrCl_4$, VF_5 [7] (Scheme 2).

A more beneficial method of telogen synthesis, which relies on the reaction of a perfluoroalkene with iodine and potassium fluoride was introduced by Krespan [8,9]. The other group of methods is based on the reaction of perfluoroalkene with iodine and hydrogen fluoride in the presence of oxidizing agents [10,11] as well as the decarboxylation of silver salts of perfluorocarboxylic acid in the presence of iodine. However, these methods are of smaller importance [12].

The first work concerning the telomerization of TFE in the presence of iodine derivatives, e.g. CF_3CCl_2I, as telogens was reported by Hauptschein and co-workers [13–15]. The processes were carried out batchwise at temperatures of 120–160 °C, at the pressures up to 70 atm over the time of 1–20 h in the absence of peroxide initiators (thermal initiation). More recently, a comprehensive review of the telomerization methods was presented by Ameduri et al. [16].

The telomers of TFE can be used in a wide range of processes as solid lubricators and anti-adhesive agents, finishing ingredients, heat transfer agents [15,17,18]. Some of the practical applications of telomers especially in the production of the surface-active agents for galvanizing bath and fire-extinguishing agents are given in [19].

Although the methods of telomerization are known, the descriptions of the telomerization of TFE are based only on the patent literature, and do not discuss the influence of technological parameters on the course of this process. The aim of this work was to establish the effect of the technological

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* Corresponding author. Tel.: +48 91 449 48 91; fax: +48 91 449 43 65.
E-mail address: Grzegorz.Lewandowski@ps.pl (G. Lewandowski).

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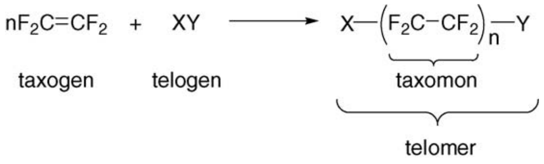


$$nF_2C{=}CF_2 + XY \longrightarrow \underbrace{X{-}\underbrace{(F_2C{-}CF_2)_n}_{\text{taxomon}}{-}Y}_{\text{telomer}}$$

taxogen telogen

Scheme 1.

$$5R_fF_2C{=}CF_2 + 2I_2 + IF_5 \longrightarrow 5R_f(CF_3)CFI$$

Scheme 2.

$$CF_3FC{=}CF_2 + KF + I_2 \longrightarrow CF_3CFICF_3 + KI$$

Scheme 3.

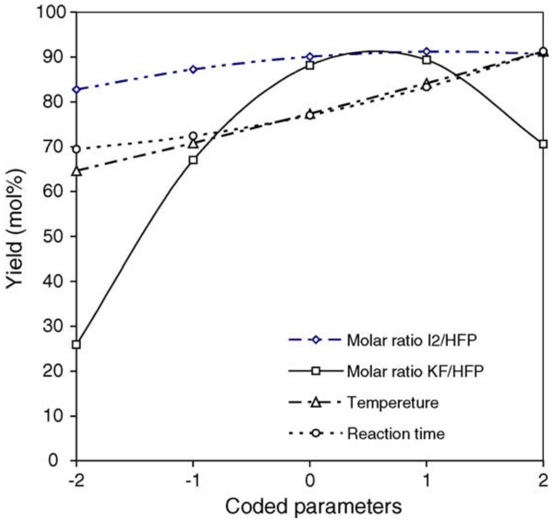


Fig. 1. The influence of the technological parameters (in the coded form) on the yield of 2-iodoheptafluoropropane. Real values of parameters are presented in Table 1.

parameters and the optimum parameters of the telomerization of TFE as well as the optimum parameters for the synthesis of telogens: 1-chloro-2-iodohexafluoropropane and 2-iodoheptafluoropropane using statistical methods of experimental design.

2. Results and discussion

2.1. Synthesis of telogens

2.1.1. Synthesis of 2-iodoheptafluoropropane

The synthesis of 2-iodoheptafluoropropane relies on the reaction of hexafluoropropene (HFP) with iodine and potassium fluoride in acetonitrile (Scheme 3) (Krespan's method [8]).

Preliminary investigations revealed that the yield of 2-iodoheptafluoropropane is influenced by parameters such as: iodine/HFP and potassium fluoride/HFP molar ratios, temperature and reaction time (independent variables). For the optimization of the 2-iodoheptafluoropropane synthesis the experiments were performed according to quaternary rotatable-uniform design of the second order. The design of experiments was performed for four independent variables established in the preliminary investigations in the following ranges of changes: X_1, I_2/HFP molar ratio (1.0–1.4); X_2, KF/HFP molar ratio (1.0–2.6); X_3, temperature (100–140 °C); X_4, reaction time (11–15 h).

The transition from the system of independent factors in the natural form to coded (dimensionless) form was performed by a linear transformation of variables:

$$x_i = (X_i - X_{i0})/\Delta X_i \tag{1}$$

where x_i is the coded variable value in the point of the experiment plan ($i = 1$–4), X_i the natural variable value in the point of the experiment plan ($i = 1$–4), X_{i0} the natural variable value in the central point of experiment plan, and ΔX_i is the step value along the X-axis (natural).

Table 1 presents the real and coded values of the experimental parameters of the design of experiments.

The yield of 2-iodoheptafluoropropane was assumed as the response function describing the process. It was defined as the amount of 2-iodoheptafluoropropane obtained in relation to (HFP) introduced into the autoclave.

The design of experiments, determination of coefficients of the polynomial describing the process (the yield of 2-iodoheptafluoropropane) and the statistical analysis of the results were performed using the Statistica computer program [20].

The analysis revealed that the yield of 2-iodoheptafluoropropane depends on all the technological parameters investigated. The greatest influence on the yield of 2-iodoheptafluoropropane is the KF/HFP molar ratio (Fig. 1). Its rise, from 1 (coded value −2) to 2 (coded value 0.5), results in the yield increase from 25 to 90 mol%. A further increase, in the KF/HFP molar ratio to 2.6 (coded value 2), causes lowering of the yield to 70 mol%. The rise of any other parameters from

Table 1
Real and coded values of experimental parameters of the 2-iodoheptafluoropropane synthesis

Level	Coded parameter (x_i)	Real values of parameters (X_i)			
		Molar ratio I_2/HFP	Molar ratio KF/HFP	Temperature (°C)	Reaction time (h)
Basic	0	1.2	1.8	120	13
Higher	1	1.3	2.2	130	14
Lower	−1	1.1	1.4	110	12
Star higher	2	1.4	2.6	140	15
Star lower	−2	1.0	1.0	100	11

$$CF_3FC{=}CF_2 + ICl \longrightarrow CF_3CFICF_2Cl + CF_3CFClCF_2I$$

Scheme 4.

$$2ICl \longrightarrow I_2 + Cl_2$$

$$CF_3FC{=}CF_2 + Cl_2 \longrightarrow CF_3CFClCF_2Cl$$

Scheme 5.

minimum to maximum value caused an increase in the yield of 2-iodoheptafluoropropane. The best results of the 2-iodoheptafluoropropane synthesis in the ranges of parameters changes investigated were for the following ranges of parameters: KF/HFP molar ratio (1.8–2.2), I_2/HFP molar ratio (1.33–1.40), temperature (133–140 °C), and reaction time (14.3–15.0 h). Under these conditions the yield of 2-iodoheptafluoropropane was above 85 mol%.

2.1.2. Synthesis of 1-chloro-2-iodohexafluoropropane

The synthesis of 1-chloro-2-iodohexafluoropropane involves the addition of iodine chloride to HFP according to Scheme 4 (Haupstchein's method [1]).

2-Chloro-1-iodohexafluoropropane is formed simultaneously and the following reactions proceed (Scheme 5).

The experiments were performed in the following range of changes of parameters: temperature (70–170 °C), the autoclave filling (0.64–1.05 kg dm^{-3}), molar ratio of substrates (0.78–1.3:1). The results of the GC analysis of the raw product show that the highest selectivity of 2-iodoheptafluoropropane (approximately 97 mol%) was obtained at the lowest temperature i.e. approximately 70 °C (Fig. 2). However, the conversion of HFP is rather small (55 mol%) at this temperature. The range of 100–110 °C should be considered as the optimum temperature. The high HFP conversion (approximately 87 mol%) is achieved with a relatively low content of by-products (selectivity of by-products less than 10 mol%). Rise of temperature above 110 °C increases the by-products, 2-chloro-1-iodohexafluoropropane and 1,2-dichlorohexafluoropropane (selectivity of by-products exceeds 14 mol%). A further increase in temperature causes a decrease of HFP conversion. The temperature affects the selectivity of isomers, 1-chloro-2-iodohexafluoropropane and 2-chloro-1-iodohexafluoropropane (Fig. 2). When the reaction is performed at temperature 70 °C, the ratio of isomer equal to 39 can be achieved, whereas, at temperature 170 °C the ratio of isomers amounts 5. The addition of iodine chloride to HFP can proceed according to either ionic or radical mechanism [21] as shown in Scheme 6.

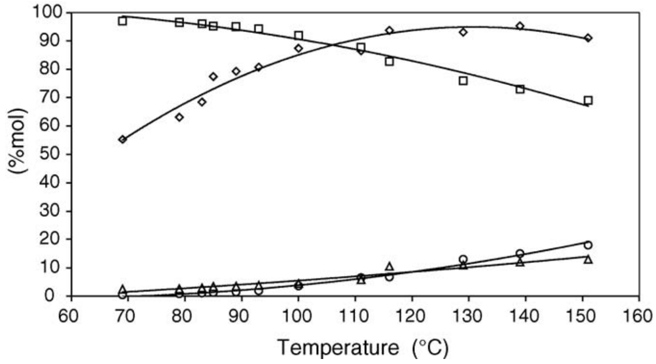
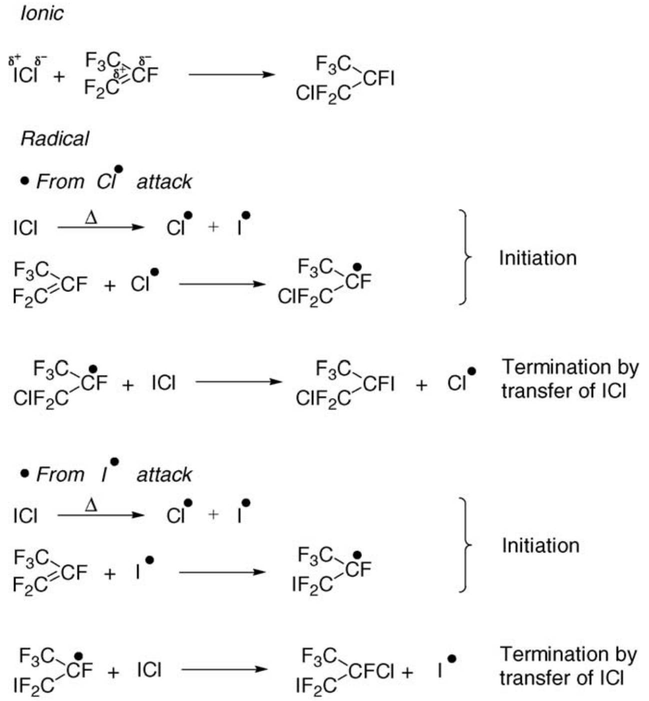


Fig. 2. The influence of the temperature on the conversion of HFP (◇) and selectivity to: 1-chloro-2-iodohexafluoropropane (□), 1,2-dichlorohexafluoropropane (○), 2-chloro-1-iodohexafluoropropane (△). Filling of the autoclave 0.75 kg dm^{-3}, molar ratio of substrates 1.15.



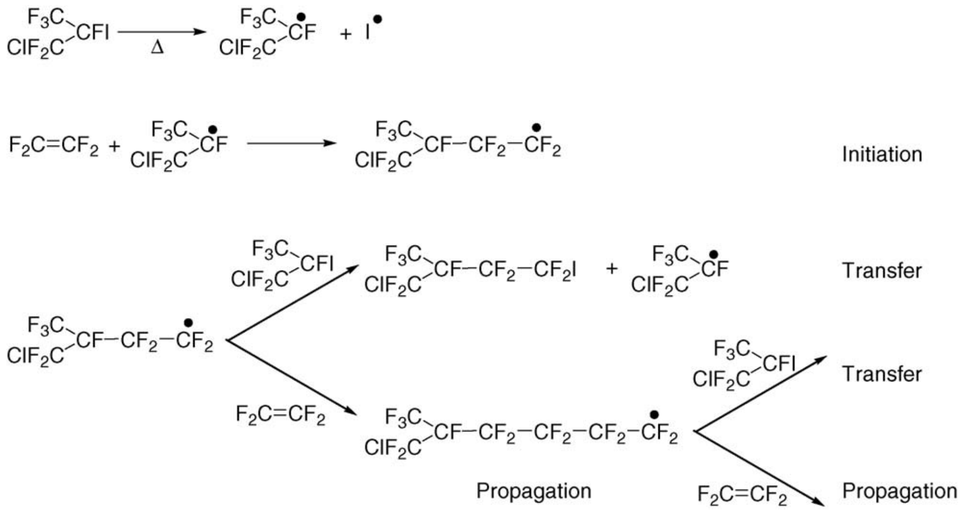
Scheme 6.

A comparison of the results of the preliminary studies (not included in this work) carried out at various autoclave filling (0.64–1.05 kg dm^{-3}) demonstrates that the best result of the 1-chloro-2-iodohexafluoropropane synthesis (HFP conversion approximately 90 mol%) was achieved at relatively high autoclave filling (approximately 0.75 kg dm^{-3}). At this autoclave filing the resulting reaction pressure (autogenic) was approximately 32 atm. Over the course of reaction, the pressure drops to approximately 9.5 atm and remains constant. About 70% of the pressure drop occurred in the first 2 h of the reaction. Enhancement of autoclave filling and consequently the reaction pressure generate a concentration effect, which probably changes the reaction kinetics and therefore the addition reaction of chlorine to HFP proceeds less intensively.

Examination of the influence of the molar ratio of substrates shows that the most advantageous is the ratio of iodine chloride to HFP from 1.1 to 1.15:1. At this molar ratio and at temperatures of 100–110 °C, the HFP conversion amounts 86–92 mol% and the yield of 1-chloro-2-iodohexafluoropropane was 77–79 mol%.

2.2. Telomerization of tetrafluoroethene

Thermal or radical initiation by AIBN or BP was employed for telomerization. The technological parameters of the process



Scheme 7.

in the preliminary experiments were as follows: the molar ratio of 1-chloro-2-iodohexafluoropropane (telogen) to TFE (taxogen) as 1:1, autoclave filling 1 kg dm^{-3}. For the radical initiation process the reaction was performed at a temperature chosen at which their half-live were close to 1 h: AIBN 78 °C, BP at 140 °C. For the reactions with thermal initiation a temperature of 150 °C and telomerization time 18 h was used. Additionally, in each experiment the taxogen pressure was controlled because it is an important parameter of the telomerization reactions.

The thermally initiated process reaction commenced after 360 min. Application of the initiators: AIBN or BP (0.05–1.00 wt.%) decreased this time to about 60 min. Typical latency times are on the order of 1–2 h for $R_fCF_2^{\bullet} + CH_2 = CH_2$ and 2–3 h for $CF_2 = CF_2$. This is a clear indication of the difficulty to propagate a radical with a taxogen containing an increasing number of F atoms. An essential difference occurs in the telomer composition. The fraction of telomers n9–n15 amounted to about 10 mol% in the thermally initiated process. In the process initiated by AIBN or BP these telomers were not formed or were formed in an amount up to 2 mol%. However, in the case when the radical initiators were used the resulting reaction pressure was unexpectedly high (300 atm) in some experiments, probably as a result of an initiator decomposition. Telogen in the form of 2-iodoheptafluoropropane, acted in the same manner as 1-chloro-2-iodohexafluoropropane. Straight-chain telomers are formed exclusively, in accordance with the general mechanism of the radical telomerization [22] (Scheme 7) independently of the telomerization method.

The formation of additional compounds was found only in the case of an initiator (BP) concentration of 1 wt.%. On the basis of both the GC-MS analysis and the elementary analysis the presence of iodine can be excluded. The compound comprises a derivative of the initiator, BP. Taking into consideration a relatively high danger associated with application of radical initiators as well as the formation of additional compounds, the thermal initiation method was used in further optimization studies.

In order to determine of the activation energy E the studies were conducted at 110, 130, 150, and 170 °C. These experiments were monitored by GC and conversions of 1-chloro-2-iodohexafluoropropane (α) to telomers: n1–n4 were determined. Approximately values of the activation energy E were calculated according to equation [23]:

$$E = -2.3RA \tag{2}$$

where E is the activation energy (J mol^{-1}), R the gas constant (8.314 J mol^{-1} deg^{-1}), A the slope of the straight lines of a plot of log α versus $1/T$.

A plot of log α versus $1/T$ (where T represents temperature) decreased linearly (Fig. 3) and the slopes of the straight lines (A) provides the activation energy E of thermal mono- di-, tri-, and terta-addition of 1-chloro-2-iodohexafluoropropane onto TFE, respectively: n1, E = 12.5 kJ mol^{-1}; n2, E = 13.6 kJ mol^{-1}; n3, E = 15.3 kJ mol^{-1}; E = 16.2 kJ mol^{-1}. These results confirm the

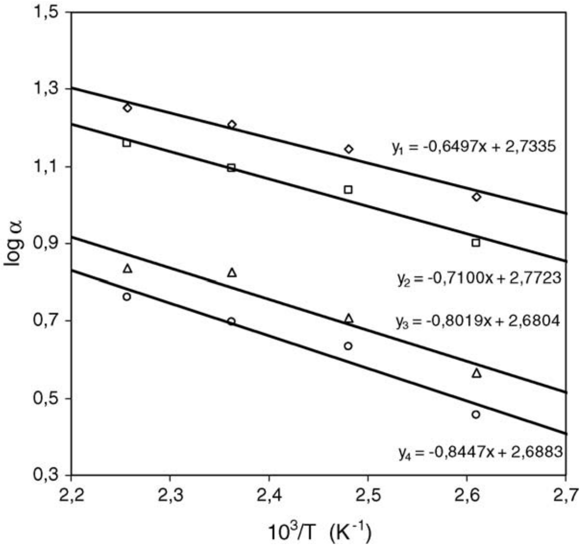


Fig. 3. Plot of log α vs. $1/T$: n1 (◇), n2 (□), n3 (△), n4 (○).

Table 2
The design matrix and the experimental value of the response functions of the TFE telomerization with 1-chloro-2-iodohexafluoropropane

No.	x_1	x_2	x_3	Y_{1-4}	Y_{2-4}
1	−1	−1	−1	12.6	9.1
2	+1	−1	−1	44.1	24.4
3	−1	+1	−1	31.0	13.0
4	+1	+1	−1	17.6	7.5
5	−1	−1	+1	35.0	22.2
6	+1	−1	+1	43.0	27.0
7	−1	+1	+1	48.5	23.5
8	+1	+1	+1	18.9	10.0
9	0	0	0	30.2	17.0
10	0	0	0	32.0	17.7
11	0	0	0	31.3	16.6

x_1, temperature; x_2, molar ratio of telogen to taxogen; x_3, reactor filling; reaction time was 18 h in all experiments; Y_{2-4}, yield of telomers n2–n4; Y_{1-4}, yield of telomers n1–n4 (response functions describing the process).

result obtained by Tedder and co-workers [24,25] for mono-addition of perfluoroalkyl iodides onto TFE ($E = 14.3$ kJ mol^{-1}).

Optimization of the technological parameters (independent variables) of TFE (taxogen) telomerization using 1-chloro-2-iodohexafluoropropane (telogen) and thermal initiation method was performed in the following ranges of changes of parameters: X_1, temperature (110–170 °C); X_2, molar ratio of telogen to taxogen of (0.7–1.2); X_3, reactor filling (0.7–1.5 kg dm^{-3}). The reaction time was 18 h in all experiments. The transition from the system of independent factors in the natural form to the coded (dimensionless) form was performed according to equations:

$$x_1 = 0.0333(X_1 - 110.0) - 1 \tag{4}$$

$$x_2 = 4.0000(X_2 - 0.7) - 1 \tag{5}$$

$$x_3 = 2.5000(X_3 - 0.7) - 1 \tag{6}$$

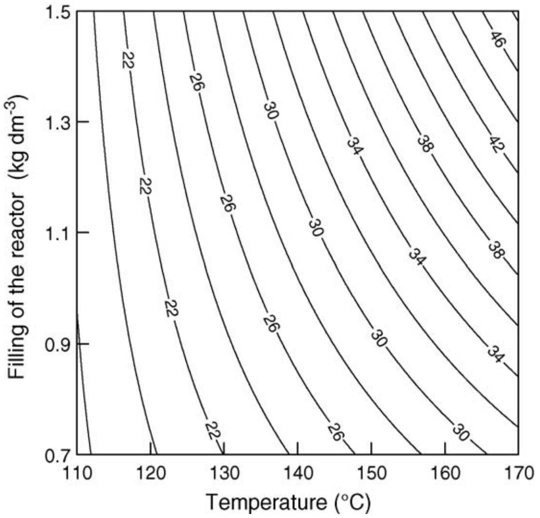


Fig. 4. The influence of the temperature and filling of the reactor on the yield of n1–n4 telomers: reaction time 18 h, telogen/taxogen molar ratio 0.7.

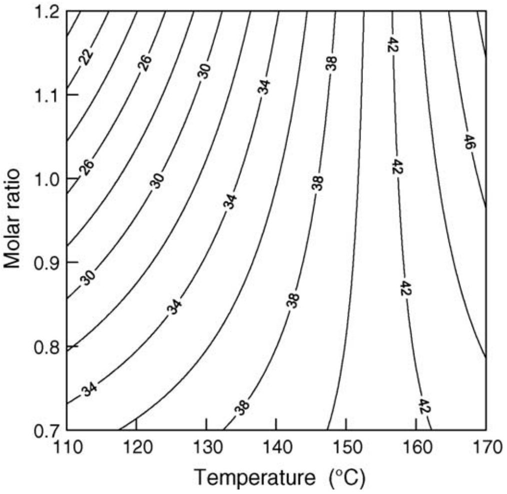


Fig. 5. The influence of the temperature and telogen/taxogen molar ratio on the yield of n1–n4 telomers: reaction time 18 h, filling of the reactor 1.5 kg dm^{-3}.

where x_i is the coded variable value in the point of the experiment plan ($i = 1–3$), and X_i is the natural variable value in the point of the experiment plan ($i = 1–3$).

The yield of telomers n2–n4 (Y_{2-4}) and the yield of telomers n1–n4 (Y_{1-4}) were assumed as the response functions describing the process. Experiments were performed with the application of three factors, three-level design of the first order. The design matrix in coded form (x_i) and the experimental value of the response functions are presented in Table 2.

Figs. 4–6 present the influence of changes of parameters on the course of Y_{1-4} function in the system of two independent variables system, the third independent variable determining the maximum of $Y_{1-4}^{\max}$ function. The courses of the yield lines in Figs. 4–6 indicate a significant influence of temperature and a less significant effect of the reactor filling and molar ratio of telogen to taxogen. A rise of temperature increases the yield of TFE telomers. The effect of a larger filling of the reactor is of a smaller importance. An increase in the yield caused by

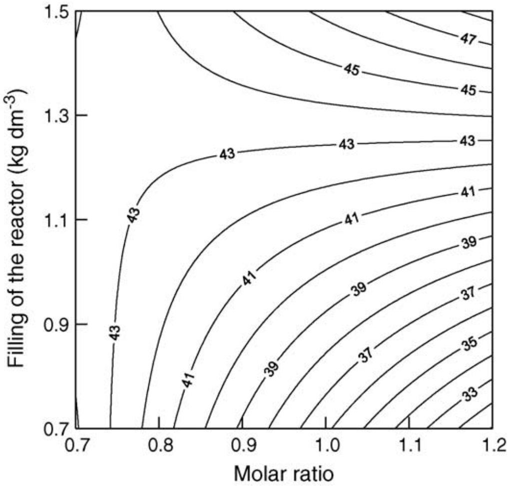


Fig. 6. The influence of telogen/taxogen molar ratio and filling of the reactor on the yield of n1–n4 telomers: reaction time 18 h, temperature 170 °C.

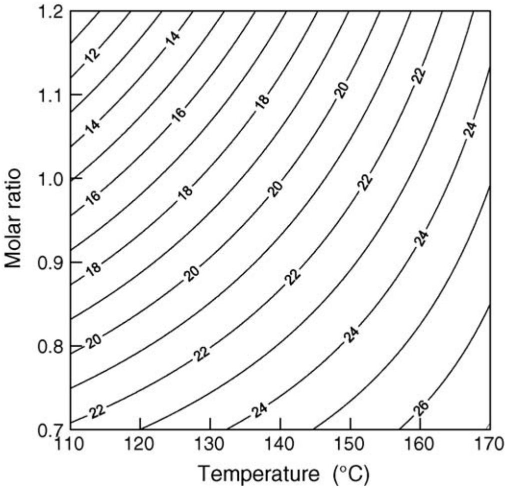


Fig. 7. The influence of the temperature and telogen/taxogen molar ratio on the yield of n2–n4 telomers: reaction time 18 h, filling of the reactor 1.5 kg dm^{-3}.

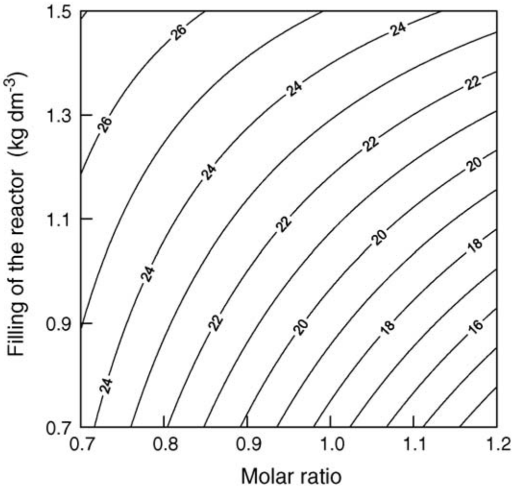


Fig. 9. The influence of telogen/taxogen molar ratio and filling of the reactor on the yield of n2–n4 telomers: reaction time 18 h, temperature 170 °C.

increasing the reactor filling is greater at higher temperatures and higher telogen/taxogen molar ratios. The above result may be explained by a concentration effect caused by increased reaction pressure, especially at higher temperatures, which probably changes the reaction kinetics as was observed for telogen synthesis from ICl and HFP. An increase of the resulting reaction pressure was approximately 30–65 atm at the start of reaction.

The influence of technological parameters on the course of Y_{2-4} function in the process with the use of 2-iodoheptafluoropropane telogen is presented in Figs. 7–9.

The isolines in Figs. 7–9 indicate that independent parameters established in the preliminary investigations influence significantly the yield of telomers n2–n4. The temperature and molar ratio of reagents appear to be great importance in achieving high yields of telomers. At the reactor filling 1.5 kg dm^{-1} and at temperature 170 °C an increase in the telogen/taxogen molar ratio from 0.7 to 1.2 lowers slightly the yield of n2–n4 telomers from 27 to 24 mol% (Fig. 7). This indicates that the telomer yield is relatively high and does not change markedly with the changes in the telogen/taxogen molar ratio at the optimum temperature. There is no need to carry out the telomerization at 170 °C as the satisfactory yields of telomers n2–n4 are achieved at 130–140 °C at the optimum telogen/taxogen molar ratio equal to 0.7 and at the optimum reactor filling 1.5 kg dm^{-1}. Such regularity can be seen for all the parameters investigated (Figs. 8 and 9).

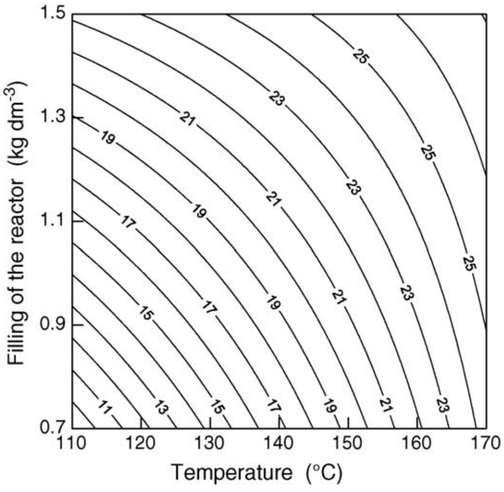


Fig. 8. The influence of the temperature and filling of the reactor on the n2–n4 telomers yield: reaction time 18 h, telogen/taxogen molar ratio 0.7.

On the basis of analysis of function Y_{2-4} it can be concluded that the telomerization process seems to be relatively simple from the technological point of view. Even a considerable change of one of the technological parameters does not cause a marked reduction of the yield of the telomers n2–n4, provided that the remaining parameters are maintained at the optimum level. However, a simultaneous change of two parameters, even when the third parameter is maintained at the optimum level, causes a rapid decrease of the value of function Y_{2-4} (Figs. 7–9).

The highest yield of telomers n2–n4 ($Y_{2-4}^{\max} = 27\,\mathrm{mol\%}$) was achieved under the conditions presented in Table 3. In a comparison with the conditions ensuring the highest yield of telomers n1–n4 ($Y_{1-4}^{\max} = 48\,\mathrm{mol\%}$) it is necessary to apply a lower molar ratio of telogen to taxogen (0.7). Under the conditions of the highest yield of telomers n1–n4 ($Y_{1-4}^{\max}$) the yield of n2–n4 amounted to 24 mol%. Under the conditions of the highest yield of telomers n2–n4 ($Y_{2-4}^{\max}$) the yield of n1–n4 amounted to 43 mol%.

Table 3
Maximum value of the response functions of the TFE telomerization with 1-chloro-2-iodohexafluoropropane

	Maximum function value	Temperature (K)	Molar ratio of telogen to taxogen	Reactor filling (kg mol^{-1})
$Y_{1-4}^{\max}$	48.4	443	1.2	1.5
$Y_{2-4}^{\max}$	27.0	443	0.7	1.5

$Y_{2-4}^{\max}$, maximum yield of telomers n2–n4; $Y_{1-4}^{\max}$, maximum yield of telomers n1–n4.

3. Conclusions

The most useful telomers of tetrafluoroethene n2–n4 can be prepared with maximum yield of 27 mol% under conditions of thermal initiation at 170 °C and at the autogenic pressure (maximum 65 atm), at the molar ratio of 1-chloro-2-iodohexafluoropropane (telogen) to tetrafluoroethene (taxogen) of 0.7, and autoclave filling of 1.5 kg dm^{-3}. Elevations of the molar ratio of telogen to taxogen to 1.2 increase significantly the amount of telomer n1 and the yield of telomes n1–n4 increases to maximum of 48 mol%. Although the most useful products of the technological process are n2–n4 telomers, their maximum yield is relatively low (27 mol%) in comparison to the maximum yield of n1–n4 telomers (48 mol%). Thus, it is advisable to carry out the process under the $Y_{1-4}^{\max}$ conditions utilizing n1 telomers or recycling them to the process.

4. Experimental

4.1. Raw materials

TFE and HFP were prepared by the pyrolysis of waste PTFF in accordance with the literature description [26]. Iodine, KF, ICl were purchased from POCh Gliwice, Poland; 2,2′-azobis(isobutyronitrile) (AIBN) and benzoyl peroxide (BP) from Fluka.

4.2. TFE handling

Handling with more than a few grams of the TFE, outside of a barricaded facility should never be considered. The spontaneous and violent (explosive) exothermic homopolymerization of TFE may take place. In addition, the monomer can undergo a very exothermic disproportionation, which is difficult to inhibit except by dilution. Moreover, highly toxic fumes of perfluoroisobutene are emitted. In any case one must never exceed a partial pressure of 20 atm of TFE in the gas phase at 20 °C.

TFE should be handled in such a way that air or oxygen will not be introduced into the system. Material that has been vaporized from the cylinder source should not be collected and stored without the addition of inhibitor.

4.3. General procedure for the telomerization

Telomerization was performed in the high-pressure autoclave made of chromium–nickel–molybdenum steel of 1 dm^3 capacity. Mixing of the reactor content proceeded as a result of the swinging motion. A known (fixed) amount of telogen was introduced to the autoclave. The autoclave was cooled to temperature of −80 °C. The temperature was regulated and controlled by means of a thermocouple placed in a thermometric well in the furnace wall. After the crystallization of telogen, the air was removed from the autoclave by means of oil vacuum pump (1 Torr). From a tank cooled in the liquid nitrogen a known amount of TFE was distilling off into the autoclave. The rate of distillation was controlled so that the overpressure does not exceed 0.66 atm. Each experiment was carried out for 18 h.

At the end of the reaction the autoclave was cooled down and the product was analysed by GC. The mass balance was performed based on the composition of the post-reactive mixture. The telomers yield and the conversion of TFE were calculated.

The consecutive telomers n1–n4 were separated from the post-reactive mixture using a Fischer distillation column containing 70 theoretical plates. The purity of prepared telomers was verified by GC and at least 98.8% of purity was achieved. The basic physicochemical properties of obtained telomers were presented in Tables 4 and 5 and compared with literature value. Tails containing more than four taxomons in a molecule of telomer (solid) was not separated and characterized.

Table 4
Refractive TFE telomers obtained using 2-iodoheptafluoropropane as telogen

No.	Telomer	B.p. (°C/Torr)	Literature value	Ref.	Refracting index n_D^{30}	Literature value	Ref.
1	$(CF_3)_2CFCF_2CF_2I$	94/760	94/760, 95/760	[14,15]	1.3375[a]	1.3370[a]	[14]
2	$(CF_3)_2CF(CF_2CF_2)_2I$	74/70	70/70, 63/48	[14,15]	1.3296	1.3298	[14]
3	$(CF_3)_2CF(CF_2CF_2)_3I$	69/52	101.5/70, 83/23	[14,15]	1.3287	1.3290	[14]
4	$(CF_3)_2CF(CF_2CF_2)_4I$	91/68	125/70, 111/23	[14,15]	1.3910	1.3914	[14]

[a] n_D^{25}.

Table 5
TFE telomers obtained using 1-chloro-2-iodohexafluoropropane as telogen

No.	Telomer	B.p. (°C/Torr)	Literature value	Ref.	Refracting index n_D^{28}	Literature value	Ref.
1	$CF_3(CF_2Cl)CFCF_2CF_2I$	45–47/40	45/40	[14]	1.3636	1.3638	[14]
2	$CF_3(CF_2Cl)CF(CF_2CF_2)_2I$	78–79/36	78/36	[14]	1.3554	1.3552	[14]
3	$CF_3(CF_2Cl)CF(CF_2CF_2)_3I$	106–107/34	106/34	[14]	1.3496	1.3492	[14]
4	$CF_3(CF_2Cl)CF(CF_2CF_2)_4I$	130–131/30	130/30	[14]	1.3387[a]	1.3390[a]	[14]

[a] n_D^{50}.

4.4. Analytical method

Quantitative analyses were performed on CHROM-5 apparatus with flame-ionization detector (FID). The column 3 m × 3 mm was made of stainless steel and the stationary phase was silicone oil 5% on Chromosorbe W-NAW (60–80 mesh). The flow rates of gases were as follows: nitrogen 30 $cm^3 min^{-1}$, air 400 $cm^3 min^{-1}$ and hydrogen 40 $cm^3 min^{-1}$. The column was operated under the conditions of a gradual increase of temperature: isothermally at 55 °C for 5 min, increase 20 °C min^{-1} up to 175 °C.

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