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Kinetics of co-polymerisation of tetrafluoroethylene with perfluoro(3,6-dioxa-4-methyl-7-octene)sulfonylfluoride

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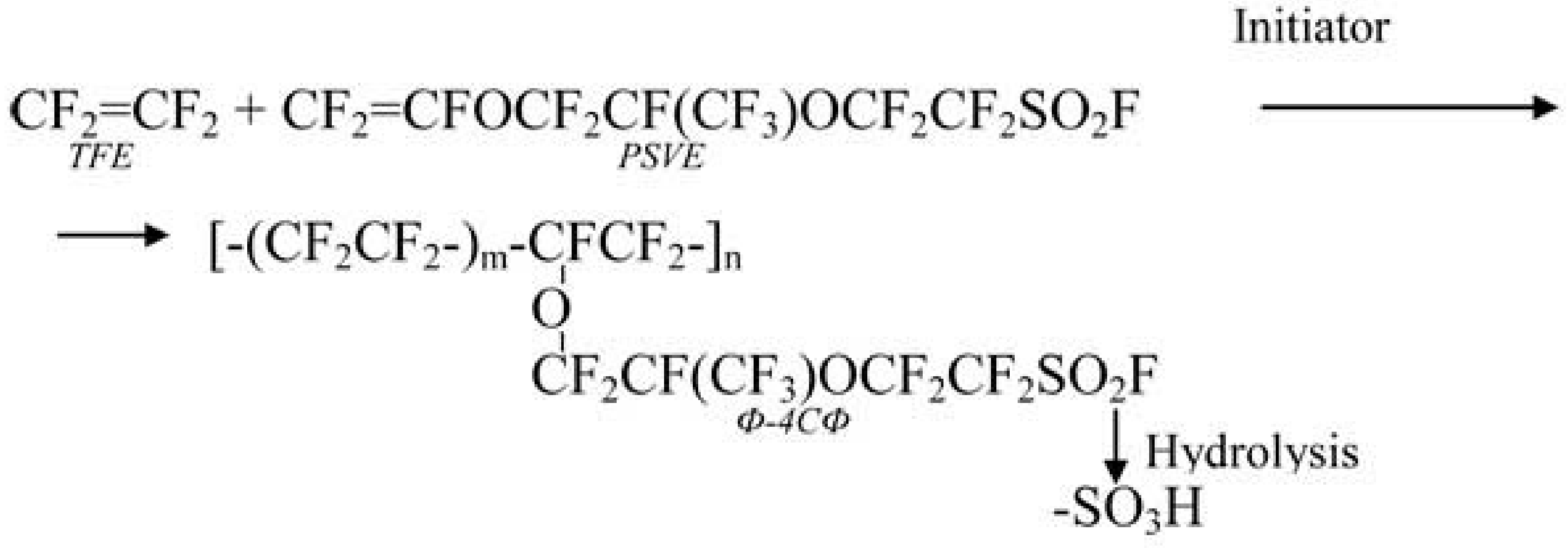
Abstract: Both temperature and monomer concentration effects on the kinetics of solution radical co-polymerisation of tetrafluoroethylene with perfluoro(3,6-dioxa-4-methyl-7-octene)sulfonylfluoride were studied.

Keywords: PSVE, perfluoro(3,6-dioxa-4-methyl-7-octene)sulfonylfluoride, tetrafluoroethylene.

Co-polymerisation of tetrafluoroethylene (TFE) and perfluoro(-3,6-dioxa-4-methyl-7-octene)sulfonylfluoride (PSVE, FC-141) results in the formation of perfluorinated co-polymer FвЂ“4SF according to the diagram as follows:



$$\underset{TFE}{CF_2{=}CF_2} + \underset{PSVE}{CF_2{=}CFOCF_2CF(CF_3)OCF_2CF_2SO_2F} \xrightarrow{\text{Initiator}} [-(CF_2CF_2-)_m-\underset{\substack{|\\O\\|\\CF_2CF(CF_3)OCF_2CF_2SO_2F\\ \Phi\text{-}4C\Phi}}{C}FCF_2-]_n \xrightarrow{\text{Hydrolysis}} -SO_3H$$

Following the film extrusion the copolymer sulfonylfluoride groups are hydrolysed to form sulfoacidic ones.

After 1960ies this well-known co-polymer is widely used in the manufacture of proton-conducting membranes (Nafion, B«Du PontB», USA; MF-4SK, Russia [1-3]).

A number of patents disclosed the methods of fluoroplast-4SF manufacture by the radical co-polymerisation in solution [4-7], in mass (without solvent) [7, 8], or by water-emulsion methods [9-17].

Earlier we have studied some aspects of TFE/PSVE co-polymerisation kinetics [18, 19]. We determined the co-polymerisation constants for TFE (r_1=9.0) and PSVE (r_2=0.04), Alfrey-Price parameters for PSVE: Q=0.02 and ГЄ=2.23, and the order of reaction by initiator n=0.7B±0.1.

The objective of this our study is to investigate both temperature and monomer concentration effects on the rate of TFE and PSVE co-polymerisation.

Experimental

Co-polymerisation was conducted in a steel 200ml reactor, equipped with a jacket and a frame stirrer (n=300 rpm). The reactor was ultra-thermostatted with accuracy B±0.1 B°C. CFC113 (1,1,2-trifluoro-1,2,2-trichloroethane) was used for solvent, and bis(perfluorocyclohexanoyl)peroxide (DAPc) was used for initiator. Tetrafluoroethylene was preliminary cleaned from inhibitor (triethylamine) in an adsorber charged with activated carbon. During the experiment the reactor pressure (and therefore, TFE concentration in liquid) was maintained constant by continuous TFE feeding from a calibrated buffer cylinder. TFE consumption was estimated by the pressure in the buffer cylinder. The polymer was washed with chloroform, and water, and then dried under vacuum at 80B°C to constant weight.

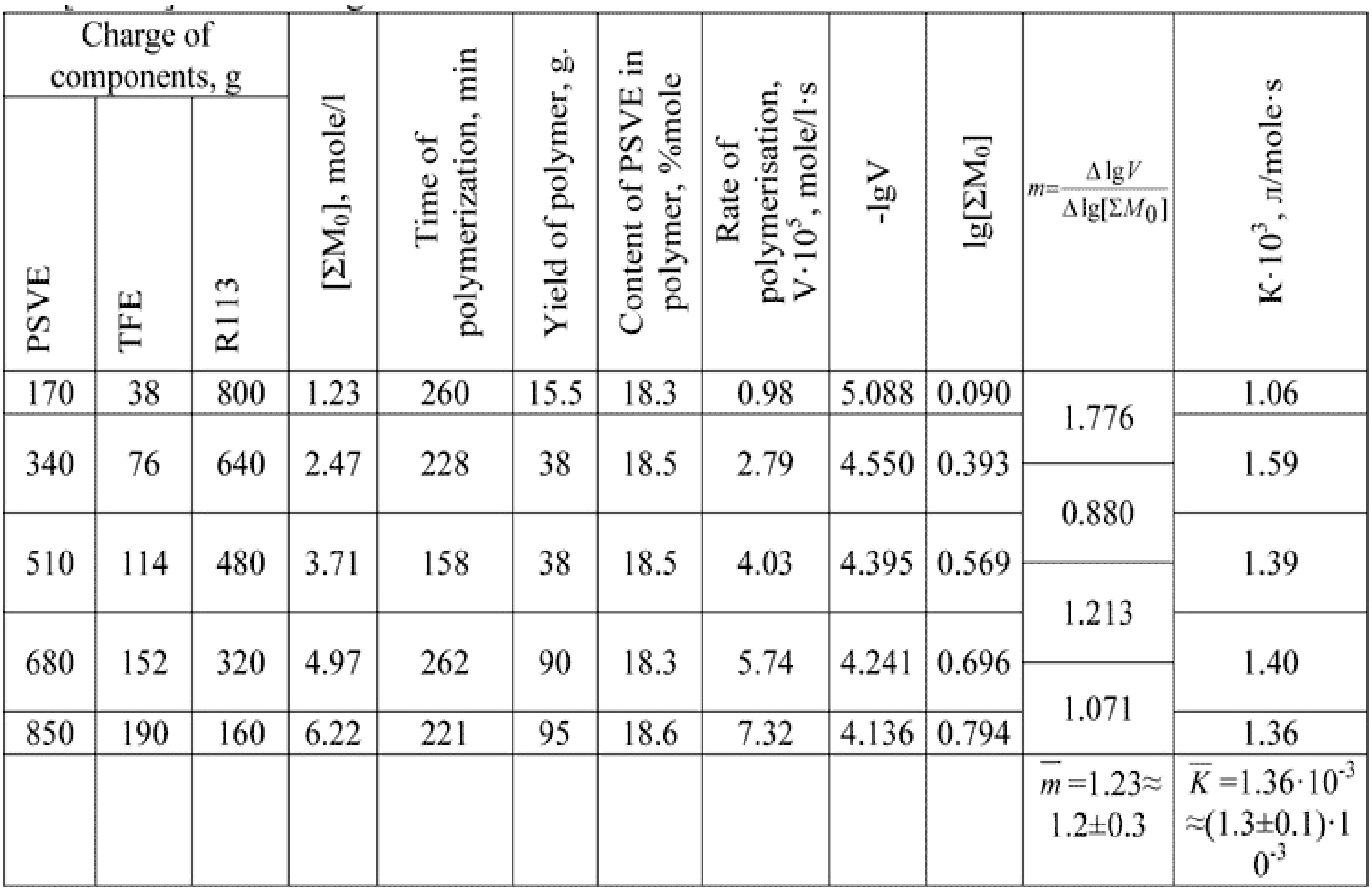
The copolymer composition was determined by the number of sulfonylfluoride groups in its IR-spectra [20], elemental analysis of sulfur content [21], and by the titration of sulfoacidic groups in hydrolysed copolymer.

The copolymer molecular mass was estimated by its melt flow index MFI with the help of a constant-pressure capillary viscosimeter (load 2.16 kg, filier diameter 2.095 mm, temperature 220Г·270B°C).

All tests were conducted at initial equimolar concentration ratio of the monomers TFE:PSVE = 1:1, and the initiator original concentration 6.7B·10^{-4} mole/l.

The results are shown in Tables 1, 2 and Figure 1.

Table 1. The dependence of TFE/PSVE co-polymerisation rate on the monomer concentrations in CFC -113 environment at 35B°C, mole ratio TFE:PSVE=1:1, and [DAPc] initiator original concentration 6.7B·10^{-4} mole/l.



Charge of components, g			$[\Sigma M_0]$, mole/l	Time of polymerization, min	Yield of polymer, g.	Content of PSVE in polymer, %mole	Rate of polymerisation, $V \cdot 10^5$, mole/l·s	-lgV	$\lg[\Sigma M_0]$	$m=\frac{\Delta \lg V}{\Delta \lg[\Sigma M_0]}$	$K \cdot 10^3$, л/mole·s
PSVE	TFE	R113									
170	38	800	1.23	260	15.5	18.3	0.98	5.088	0.090	1.776	1.06
340	76	640	2.47	228	38	18.5	2.79	4.550	0.393	0.880	1.59
510	114	480	3.71	158	38	18.5	4.03	4.395	0.569	1.213	1.39
680	152	320	4.97	262	90	18.3	5.74	4.241	0.696	1.071	1.40
850	190	160	6.22	221	95	18.6	7.32	4.136	0.794		1.36
										$\overline{m}=1.23\approx 1.2\pm0.3$	$\overline{K}=1.36\cdot10^{-3} \approx(1.3\pm0.1)\cdot10^{-3}$

The co-polymerisation was depicted by a simplified equation as follows:

V=KB·[DAPc]^{n}B·[в€‘M$_0$]^{m}, mole/lB·s B B B (1)

here: Рљ is effective rate constant of the co-polymerisation process, mole/l;
[DAPc] is the concentration of initiator, mole/l;
[в€‘M$_0$] is combined initial concentration of the monomers, mole/l;
n is the reaction order by initiator;
m is the reaction order by the combined concentration of the monomers.

The reaction order by monomers was determined for each pair of tests according to the equation (2), derived according to the diagram as follows:

V$_1$=KB·[DAPc]$_0$^{n}B·[в€‘M$_0$]$_1$^{m};

V$_2$=KB·[DAPc]$_0$^{n}B·[в€‘M$_0$]$_2$^{m};

lgV$_1$=lgK+nlg[DAPc]$_0$+mlg[в€‘M$_0$]$_1$;

lgV$_2$=lgK+nlg[DAPc]$_0$+mlg[в€‘M$_0$]$_2$;

lgV$_1$-lgV$_2$=m(lg[в€‘M$_0$]$_1$-lg[в€‘M$_0$]$_2$), from where

$$m = \frac{\Delta \lg V}{\Delta \lg[\Sigma M_0]} \qquad (2)$$

The effective rate constant of co-polymerisation was calculated by the equation (3):

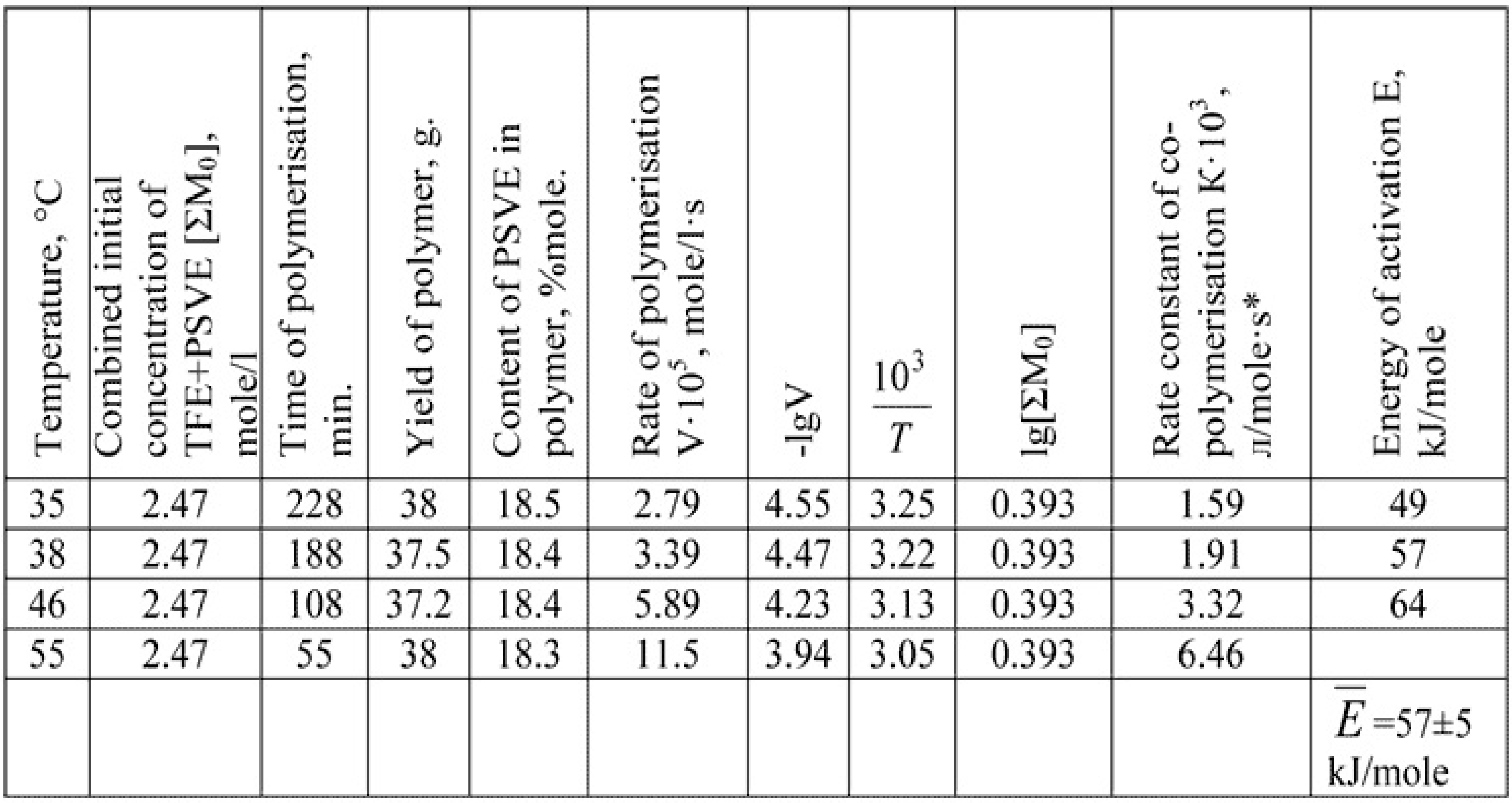
$$K = \frac{V}{[\mathrm{DAPc}]_0^{0,7} \cdot [\Sigma M_0]^{1,2}}\text{, l/mole}\cdot\text{s} \qquad (3)$$

Reasoning from the experimental (Table 1) and published results [19] for TFE /PSVE co-polymerisation in CFC113 at 35B°C the equation (1) is:

V=(1.3B±0.1)B·10^{-3}B·[DAPc]$^{0.7B±0.1}$B·[в€‘M$_0$]$^{1.2B±0.3}$, mole/lB·s B B B B (4)

Our results for temperature dependence of the rate of TFE /PSVE co-polymerisation are shown in Table 2 and Figure 1.

Table 2. Temperature dependence of TFE /PSVE co-polymerisation rate in CFC113 environment at TFE:PSVE=1:1 mole ratio and the initiator initial concentration [DAPc]= 6.7B·10^{-4} mole/l.



Temperature, °C	Combined initial concentration of TFE+PSVE [ΣM_0], mole/l	Time of polymerisation, min.	Yield of polymer, g.	Content of PSVE in polymer, %mole.	Rate of polymerisation $V\cdot10^5$, mole/l·s	-lgV	$\frac{10^3}{T}$	lg[ΣM_0]	Rate constant of co-polymerisation $K\cdot10^3$, л/mole·s*	Energy of activation E, kJ/mole
35	2.47	228	38	18.5	2.79	4.55	3.25	0.393	1.59	49
38	2.47	188	37.5	18.4	3.39	4.47	3.22	0.393	1.91	57
46	2.47	108	37.2	18.4	5.89	4.23	3.13	0.393	3.32	64
55	2.47	55	38	18.3	11.5	3.94	3.05	0.393	6.46	
										$\overline{E}$=57±5 kJ/mole

Note*: Effective rate constant of co-polymerisation was calculated by equation (3).

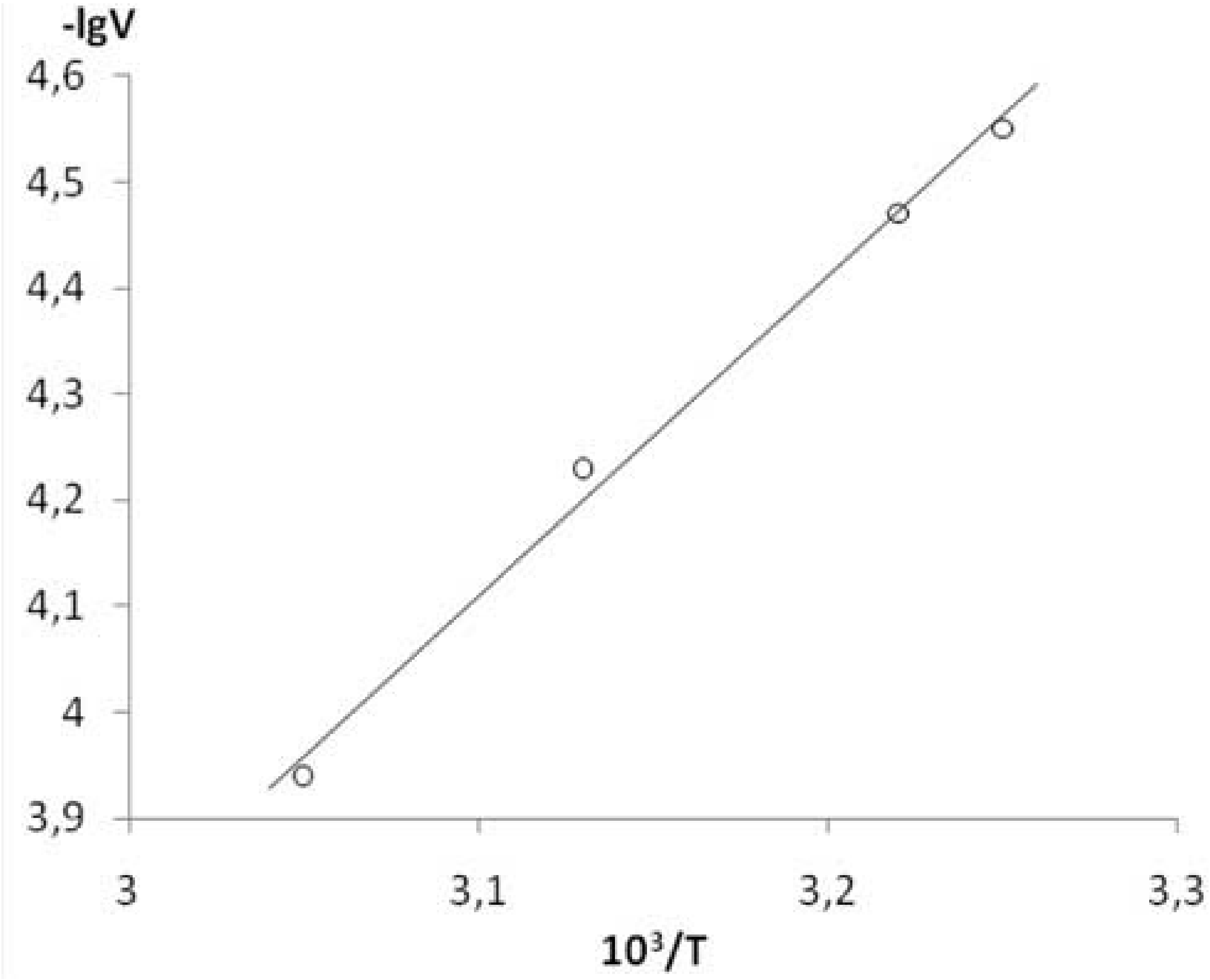


Figure 1. Temperature dependence of TFE/PSVE co-polymerisation rate in Arrhenius coordinates.

Energy of activation of TFE / PSVE co-polymerisation within temperature range 35-55 B°C is 57B±5 kJ/mole (Table 2, Figure 1).

Conclusions

1. The kinetic parameters are determined experimentally for the radical co-polymerisation of TFE /PSVE monomers, used in the manufacture of perfluorinated ion-exchange membranes.
2. he obtained values of the co-polymerisation rate constants, activation energies, reaction orders by combined monomer concentrations and by initiator concentrations are typical for the reactions of radical co-polymerisation of perfluorinated alkylvinyl ethers in solutions [8]; the process is heterogenous because F-4SF co-polymer thus formed is swelled in the reaction medium but not dissolved in it.

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