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MACROMOLECULAR CHEMISTRY AND POLYMERIC MATERIALS

Kinetics of Copolymerization of Tetrafluoroethylene with Perfluoro(3,6-dioxa-4-methyl-7-octen)sulfonyl Fluoride

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Abstract—Effect of composition of a monomers mixture on the kinetics of radical polymerization in solution of tetrafluoroethylene with perfluoro(3,6-dioxa-4-methyl-7-octene)sulfonyl fluoride is studied.

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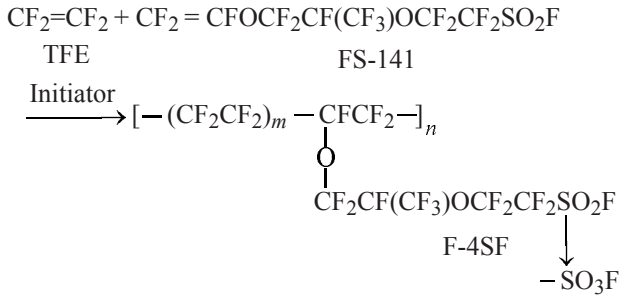
Copolymerization of tetrafluoroethylene with perfluoro(3,6-dioxa-4-methyl-7-octene)sulfonyl fluoride (FS-141) with formation of perfluorinated copolymer F-4SF proceeds along the scheme:



Sulfonyl fluoride groups of the copolymer are hydrolyzed to sulfonate ones after obtaining an extrusion film.

This copolymer is known since nineteen sixties. It is used for producing the membranes for proton transmission Nafion (Du Pont, USA) and MF-4 (Russia) [1–3].

A series of patents has been published disclosing the methods of producing fluoroplast 4SF by radical copolymerization in solution [4-7], in bulk (without a solvent) [7, 8] and by water emulsion method [9–17]. However, in literature there are no publications about the kinetics of this copolymer synthesis.

The aim of this work is the study of the effect of composition of the monomer mixture on the kinetics of radical polymerization in solution of tetrafluoroethylene and FS-141.

EXPERIMENTAL

The copolymerization was carried out in a steel reactor 200 ml capacity with a jacket and a frame stirrer (n = 300 rpm). The reactor temperature was maintained with a thermostat with accuracy of ±0.1°C. Solvent was 1,1,2-trifluoro-1,2,2-trichloroetane (X-113), initiator bis-(perfluorocyclohexanoyl)peroxide. Tetrafluoroethylene was purified from inhibitor (triethylamine) in an adsorber filled with activated carbon. During the experiment the prssuere in the reactor (and hence tetrafluoroethylene concentration in liquid phase) was maintained constant by feeding trafluoroethylene from a calibrated buffer receiver. The tetrafluoroethylene consumption was determined from the pressure change in the buffer receiver. The polymer was washed with chloroform and water and dried in a vacuum at 80°C to constant weight.

The copolymer composition was determined from the number of sulfofluorine groups elucidated by IR spectroscopy, elemental analysis on the content of sulfur [18], and by titration of sulfonate groups of the hydrolyzed copolymer. Molecular mass of the copolymer was estimated from the melt flow index (MFI) using a capillary viscometer at constant pressure (tension 2.16 kg, capillary tube diameter 2.095 mm, temperature in the range 220–270°C).

First of all, we studied solubility of tetrafluoroethylene in FS-141 and X-113 in the working temperature range (Figs.1 and 2).

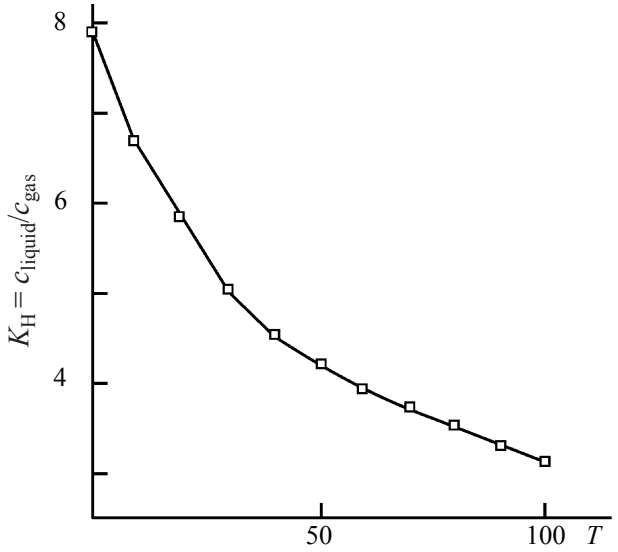


Fig. 1. Solubility of tetrafluoroethylene in FS-141.

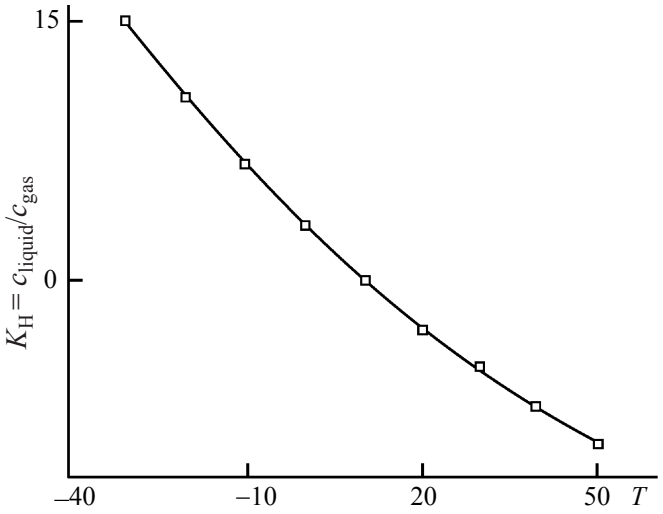


Fig. 2. Solubility of tetrafluoroethylene in X-113. $c_{gas} = P/22.4$ is tetrafluoroethylene concentration in gas phase (mol l^{-1}), P is tetrafluoroethylene pressure (atm).

The solubility was estimated from the value of Henry constant:

$$K_H = c_{liquid}/c_{gas},$$

where c_{liquid} is tetrafluoroethylene concentration in the liquid phase (mol l^{-1}), K_H is Henry constant, T is temperature (°C); the same in Fig. 2.

The tetrafluoroethylene concentration in liquid phase of the reaction mixture was estimated with the Krichevskii formula [19]

$$c_{liquid} = K'_H c_{gas},$$

where c_{gas} is tetrafluoroethylene concentration in the gas phase (mol l^{-1}), K'_H is Henry constant for the mixture FS-141 and X-113:

$$K'_H = x_1 \ln K_{H1} + x_2 \ln K_{H2},$$

where x_1 and x_2 are mole fractions of FS-141 and X-113 in the reation mixture measured by chromatography, K_{H1} and K_{H2} are Henry constants for FS-141 and X-113 at the operating temperature determined from the Figs. 1 and 2.

Then we studied dependence of the copolymer composition on the composition of the monomer mixture (Fig. 3). By the Fineman–Ross method from the data in Fig. 3 we calculated the constants of copolymerization of tetrafluoroethylene and FS-141: $r_{TFE} = 9.0$ and $r_{FS\text{-}141} = 0.04$, and the Alfrey–Price parameters for FS-141:

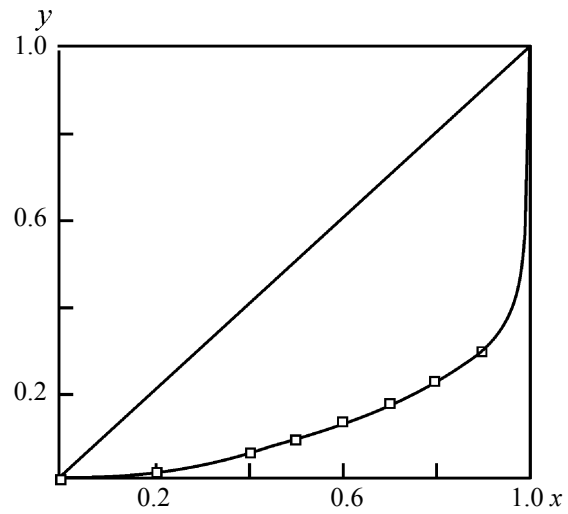


Fig. 3. Dependence of the copolymer F-4SF composition on the composition of the monomer mixture. Ratio X-113 : FS-141 = 2 : 1(wt), T = 35°C. Concentration of initiator 6.7×10^{-4} mol l^{-1}. *y, x* are contents of FS-141 in the copolymer and in monomeric mixture, respectively (mole fraction).

$Q_{FS\text{-}141} = 0.02$, $l_{FS\text{-}141} = 2.23$. For tetrafluoroethylene the Alfrey–Price parameters are known [20]: $Q_{TFE} = 0.049$, $l_{TFE} = 1.22$

The values of polymerization constants ($r_{TFE} >> 1$, $l_{FS\text{-}141} \to 0$) indicate that the copolymer should consist of tetrafluoroethylene blocks with inclusion between them of single monomer units of FS-141 [20]. Besides, with increase in content of FS-141 units in the copolymer its molecular weight should decrease as is really found in practice.

Copolymerization constants of tetrafluoroethylene (M1) with perfluorinated alkylvinyl ethers (M2) and values of Alfrey– Price parameters

M_2	r_1	r_2	r_1r_2	$\bar{l}_2$	Q_2	Conditions of polymerization		References
						T	medium	
CF_2=$CFOCF_2CF(CF_3)OCF_2CF_2SO_2F$	9.0	0.04	0.36	2.23	0.019	35	X-113	This work
CF_2=$CFOCF_2CF(CF_3)O(CF_2)_3SO_2F$	8.0	0.08	0.64	1.89	0.014	30	X-113	[21]
CF_2=$CFOCF_2CF(CF_3)O(CF_2)_3COOCH_3$	7.0	0.14	0.98	1.36	0.008	70	in bulk	[22]
CF_2=$CFO(CF_2)_3COOCH_3$	7.0	0.14	0.98	1.36	0.008	70	in bulk	[22]
CF_2=$CFOCF_2CF_2CF_3$	8.7	0.06	0.52	2.03	0.015	25–45	X-113	[23]
CF_2=$CFOCF_2CF(CF_3)OCF_2CF_2CF_3$	15.6	0.018	0.28	2.35	0.012	25–45	X-113	[23]

The obtained values of copolymerization constants are typical for the tetrafluoroethylene copolymers with polyfluorinated alkylvinyl ethers regardless the presience in the latter of functional groups and nature of these groups (see the table).

Note the enhanced values of the copolymer-ization constants of polyfluorinated alkylvinyl esters, but this fact can result from a higher polymerization temperature that leads to convergence of activity of the comonomers [24].

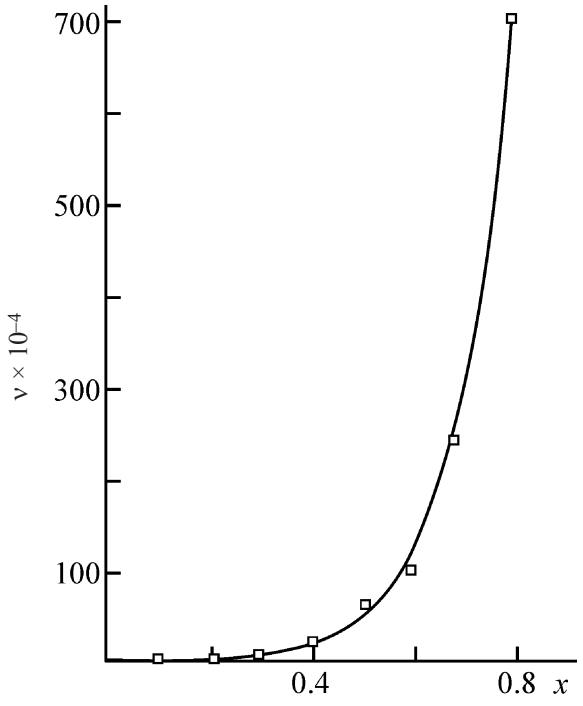


Fig 4. Plot of copolymerization rate v g l^{-1} s^{-1}) of tetrafluoroethylene with FS-141 on the composition of monomeric mixture. Initiator concentration 6.7 × 10^{-4} mol l^{-1}, T = 35°C, X-113 : FS-141 = 2 : 1 (wt), tetrafluoroethylene : FS-141 = 1 : 1 (mole). x is content of tetrafluoroethylene in the monomeric mixture (mole fraction).

The positive values of l parameter for all the considered monomers indicates electron-acceptor effect of fluorine and of perfluoroalkoxy groups. The l parameter of polyfluorinated alkylvinyl ethers is higher than that of tetrafluoroethylene (see the table), i.e., the double bond in the polyfluorinated alkylvinyl ethers is more polar than in tetrafluoroethylene, but the presence of functional groups in polyfluorinated alkylvinyl ethers does not increase the double bond polarity.

Thus, polar functional group in the molecule of perfluorinated polyfluorinated alkylvinyl ether being separated from the double bond by several methylene and ether groups does not affect substantially the radical reactivity and polarity of the C=C bond.

The dependence of copolymerization rate of tetrafluoroethylene and FS-141 on the composition of the monomeric mixture is depicted in Fig. 4. At the low content of tetrafluoroethylene in the monomeric mixture the copolymerization rate is very low, and its raises exponentially with the increase in molar fraction of tetrafluoroethylene. Such run of this plot is characteristic of the comonomers that differ considerably by their reactivity [25].

CONCLUSIONS

1. The values of copolymerization constants of tetrafluoroethylene (r = 9.0) and FS-141 (r = 0.04) indicate that the copolymer with F-4SF should consist of the blocks of tetrafluoroethylene with rare units of FS-141 monomer between them.

2. The reactivity of tetrafluoroethylene in the reaction of copolymerization is by two orders of magnitude higher than that of FS-141 resulting in exponential raise of the copolymerization rate for these monomers with the raise

in mole fraction of tetrafluoroethylene in the reaction mixture.

3. Presence in perfluorinated alkylvinyl ethers of polar groups (sulfonyl fluoride and ester) affects insignificantly their reactivity in the copolymerization with thtrafluoroethylene.

4. Solubility of tetrafluoroethylene in X-113 and FS-141 is studied that allows measuring the concentration ratio of tetrafluoroethylene and FS-141 in the liquid phase during the polymerization in solution.

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