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Stage of initiation in the process of co-polymerization of tetrafluoroethylene with perfluoro-3,6-dioxa-4-methyl-7-octenesulfonylfluoride

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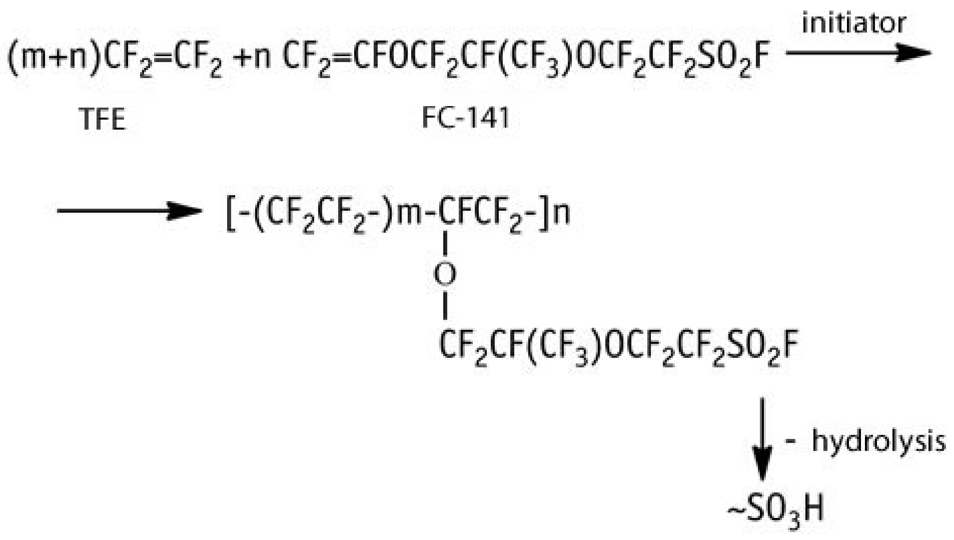
Abstract:
The initiator concentration effects on the kinetics of solution radical co-polymerization of tetrafluoroethylene with perfluoro(-3,6-dioxa-4-methyl-7-octene)sulfonylfluoride are investigated

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

Radical co-polymerization of tetrafluoroethylene (TFE) with perfluoro(3,6-dioxa-4-methyl-7-octene)sulfonylfluoride (FC-141) occurs according the following flow-diagram and results in the formation of F-4CF perfluorinated co-polymer:



$$\underset{\text{TFE}}{(m+n)CF_2{=}CF_2} + \underset{\text{FC-141}}{n\,CF_2{=}CFOCF_2CF(CF_3)OCF_2CF_2SO_2F} \xrightarrow{\text{initiator}}$$

$$\longrightarrow [-(CF_2CF_2-)m-\underset{\substack{|\\ O\\ |\\ CF_2CF(CF_3)OCF_2CF_2SO_2F}}{CF}CF_2-]n \xrightarrow{\text{- hydrolysis}} {\sim}SO_3H$$

Sulfonylfluoride groups are hydrolyzed to sulfoacid groups. F-4CF is used in the production of proton-exchange membranes for fuel cells, for alkaline-chlorine electrolysis of sodium chloride, for hydrogen production via water electrolysis, and for heterogeneous acid catalyst [1-4].

In our earlier report [5] we considered the effects of the monomer mixture composition on the kinetics of TFE /FC-141 solution co-polymerization. This study investigates the initiator concentration effects on this process.

Experiment

Co-polymerization was conducted in a stainless steel (X18H10T) reactor of volume 200ml equipped with a jacket and a frame stirrer (n=300 rpm). The reactor was thermostated with the help of an ultrathermostat with accuracy ±0,1^{o}C. 1,1,2-trifluoro-1,2,2-trichloroethane (freon-113) was used for solvent, initiator - bis(perfluorocyclohexanoyl)peroxide. Tetrafluoroethylene was cleaned from inhibitor (triethylamine) in an adsorber charged with activated carbon AG-3. The reactor pressure during the experiment (and hence TFE concentration in liquid) was kept unchanged by permanent TFE feeding from a calibrated buffer capacity. TFE consumption was determined from the pressure variation in the buffer capacity. When the depth of FC-141 conversion reached ~5% mass the polymerization process was stopped by triethylamine inhibitor introduced into the reactor. The resulting polymer was washed with chloroform and water and dried under vacuum at 60 ^{O}C to constant mass.

The copolymer composition was determined by the number of sulfofluoride groups as estimated by IR-spectroscopy [6], elemental analysis for sulfur [7], titration of sulfoacid groups of the hydrolyzed copolymer.

The co-polymer molecular mass was estimated by the maximal Newtonian viscosity (η_0) of melt copolymer according to [8]. Those η_0 values for the co-polymer samples were detected with the help of a capillary constant-pressure viscosimeter at various loads, the capillary diameter was 1,02mm, its length was 35mm, and temperature was 270^{O}C.

The rate of co-polymerization was detected by gravimetric analysis by the co-polymer yield in polymerization.

It was found experimentally that the rate of TFE/FC-141 co-polymerization grows linearly when the initiator starting concentration increases within the range (7.5-47)*10^{-4} mol*l $^{-1}$ (Fig.1), while the co-polymer equivalent weight (i.e., molecular mass per one sulfogroup) that is a characteristics of the co-polymer composition stays practically unchanged (Fig. 2).

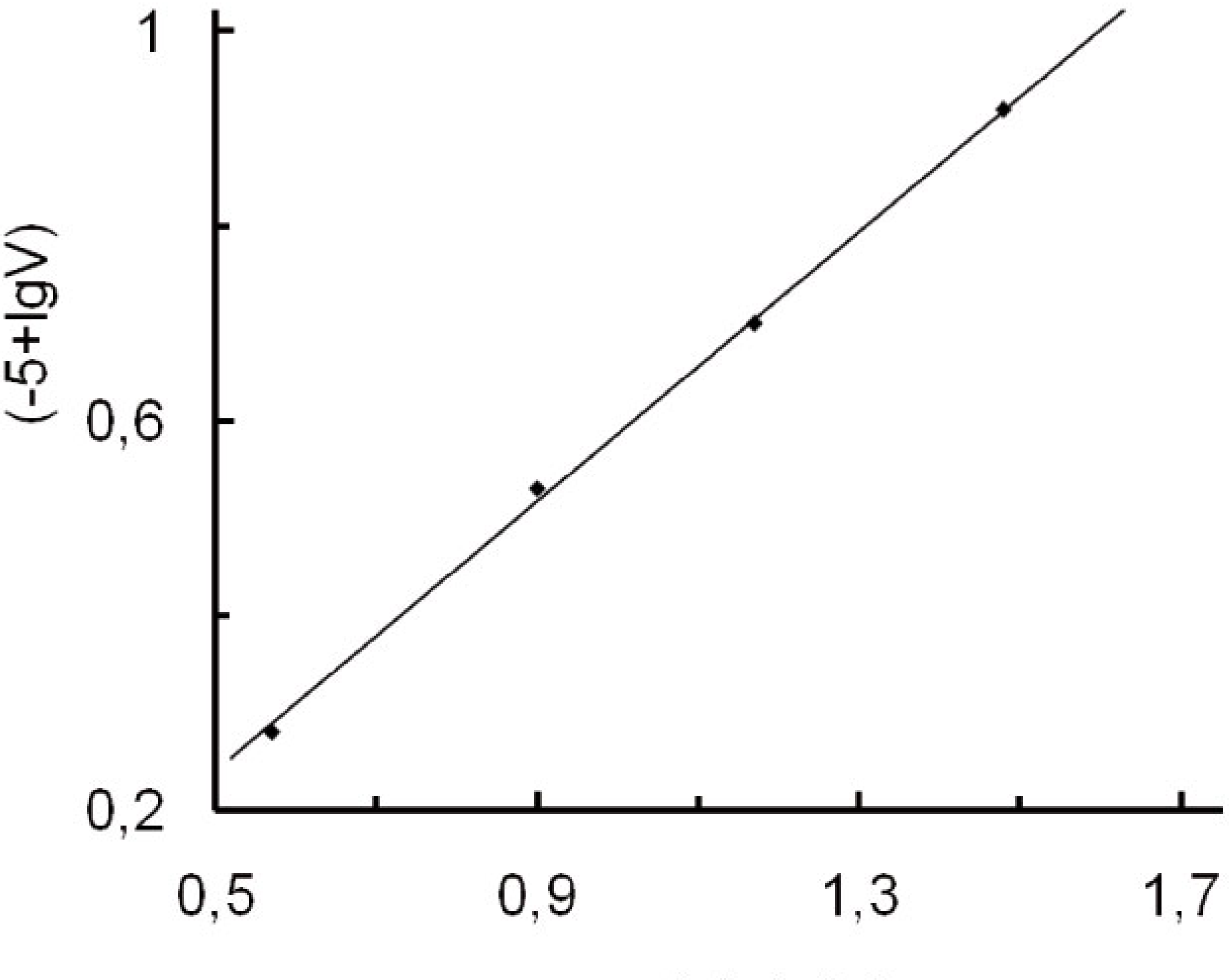


Fig. 1. *Dependence of the rate of TFE/FC-141 co-polymerization (V, mol*(l*s)$^{-1}$) on the initiator starting concentration (C$_0$, mol*l^{-1}) in logarithmical coordinates. The starting concentration of FC-141=1,2 mol*l^{-1}. The concentration of TFE=1,04 mol*l^{-1}.T=38±0,5^{O}C, P=4,1atm*

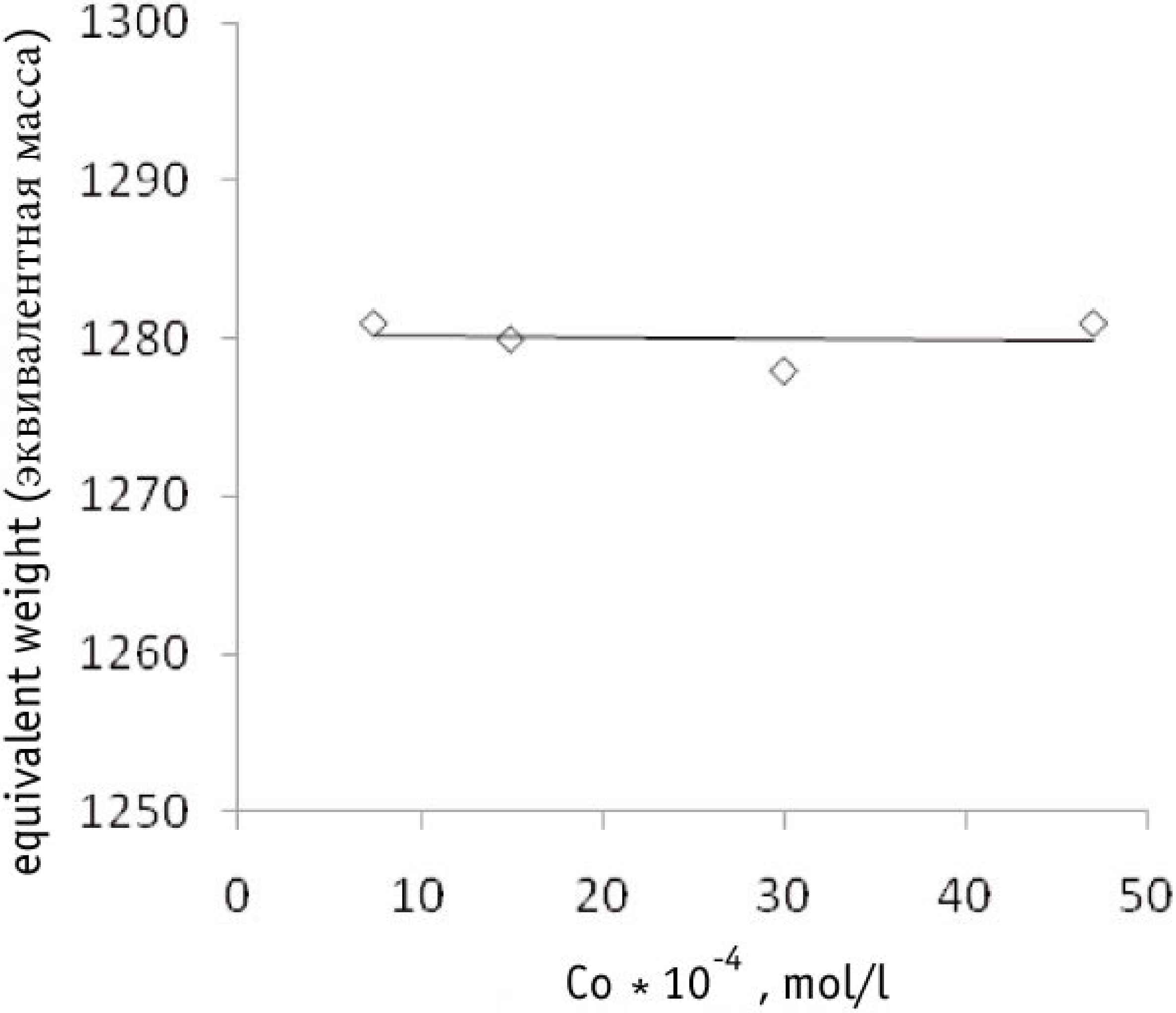


Fig.2. *Dependence of F-4CF co-polymer equivalent weight on the starting concentration of the initiator (Co, mol*l*$^{-1}$*) in the synthesis of co-polymer at 38*^{o}*C, pressure 4,1atm, FC-141/TFE ratio =1,2/1,04 (mol)*

According to the data of Fig.1 the co-polymerization reaction order (by the initiator) is n=0.7±0.1. The calculation was done by the Van't Hoff method [9, p.14] according to the formula:

$$n = \frac{\lg V_1 - \lg V_2}{\lg(c_0)_1 - \lg(c_0)_2} \quad ,$$

Here $(c_o)_1$, $(c_o)_2$, and V_1, V_2 are the starting initiator concentrations (mol*l^{-1}) and related co-polymerization rates (mol*(l*s)$^{-1}$) for points on the right line in Fig. 1.

The deviation of the reaction order from value 0.5 typical for quadratic chain termination to the side 1 associated with monomolecular chain termination is typical for polymerization followed by polymer precipitation from the solution [10]. The studied process belongs to that type of processes.

The viscosity of the studied F-4CF co-polymer samples melt at 270^{o}C does not depend on their shearing force (fig. 3), i.e. the temperature of determination of melt flow index (MFI) was appropriately chosen, melt flow was Newtonian [11, p.190] and defined the co-polymer molecular mass.

The maximal Newtonian melt viscosity (η_0) was obtained through the extrapolation of the melt flow curve (fig. 3) to the zero shearing force $\tau \rightarrow 0$.

Therefore the data of Fig. 4 testify that when the starting initiator concentration increases not only the melt viscosity but also its molecular weight go down.

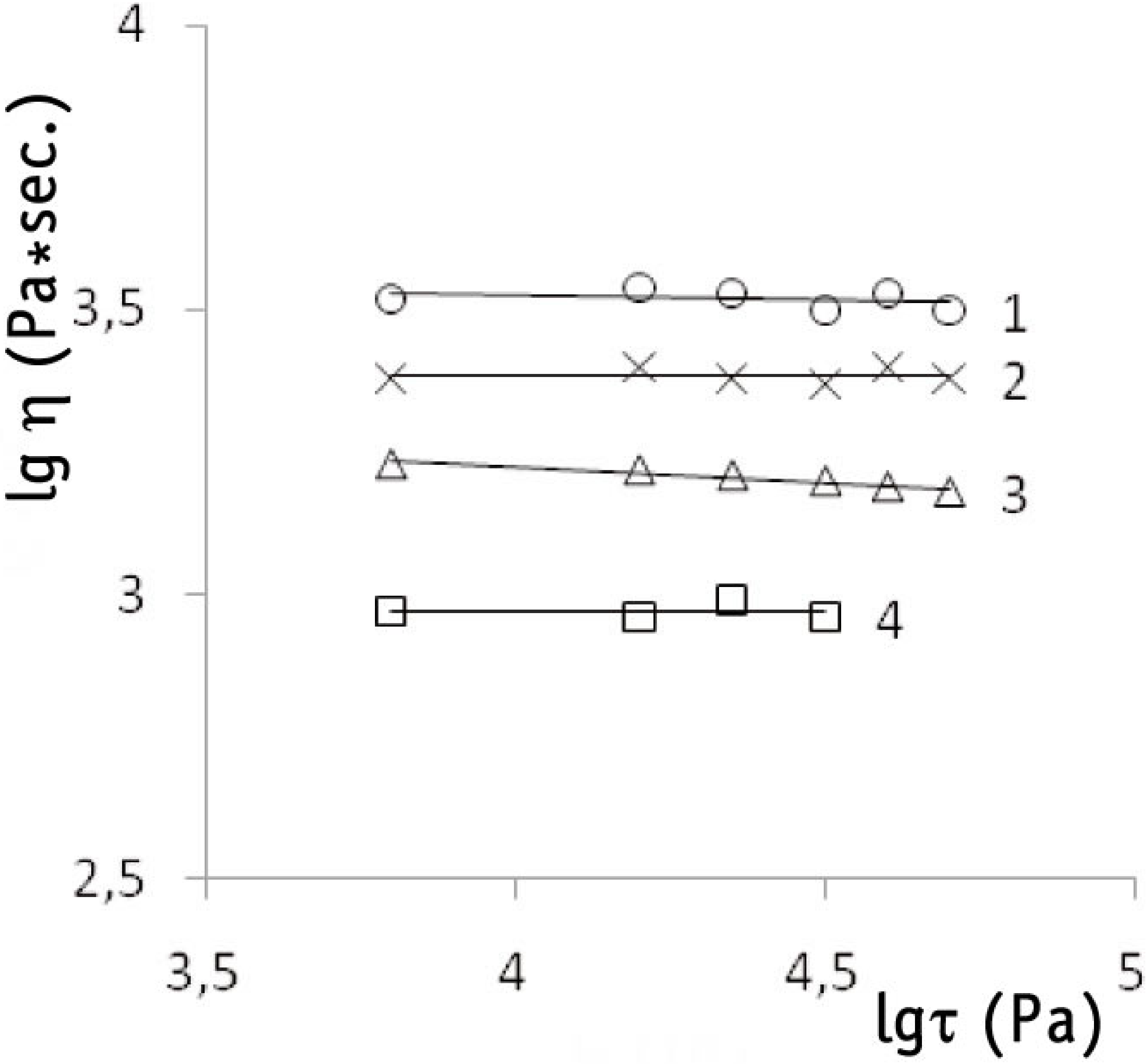


Fig. 3. *Dependence of F-4CF co-polymer melt viscosity (η, Pa*sec) at 270^{0}C on the shear stress (τ, Pa) for polymer samples produced at various starting initiator concentrations (Co).*

*1. Co=7,5*10^{-4} mol*l^{-1}.*
*2. 15,0*10^{-4} mol*l^{-1}.*
*3. 30,0*10^{-4} mol*l^{-1}.*
*4. 47,0*10^{-4} mol*l^{-1}.*

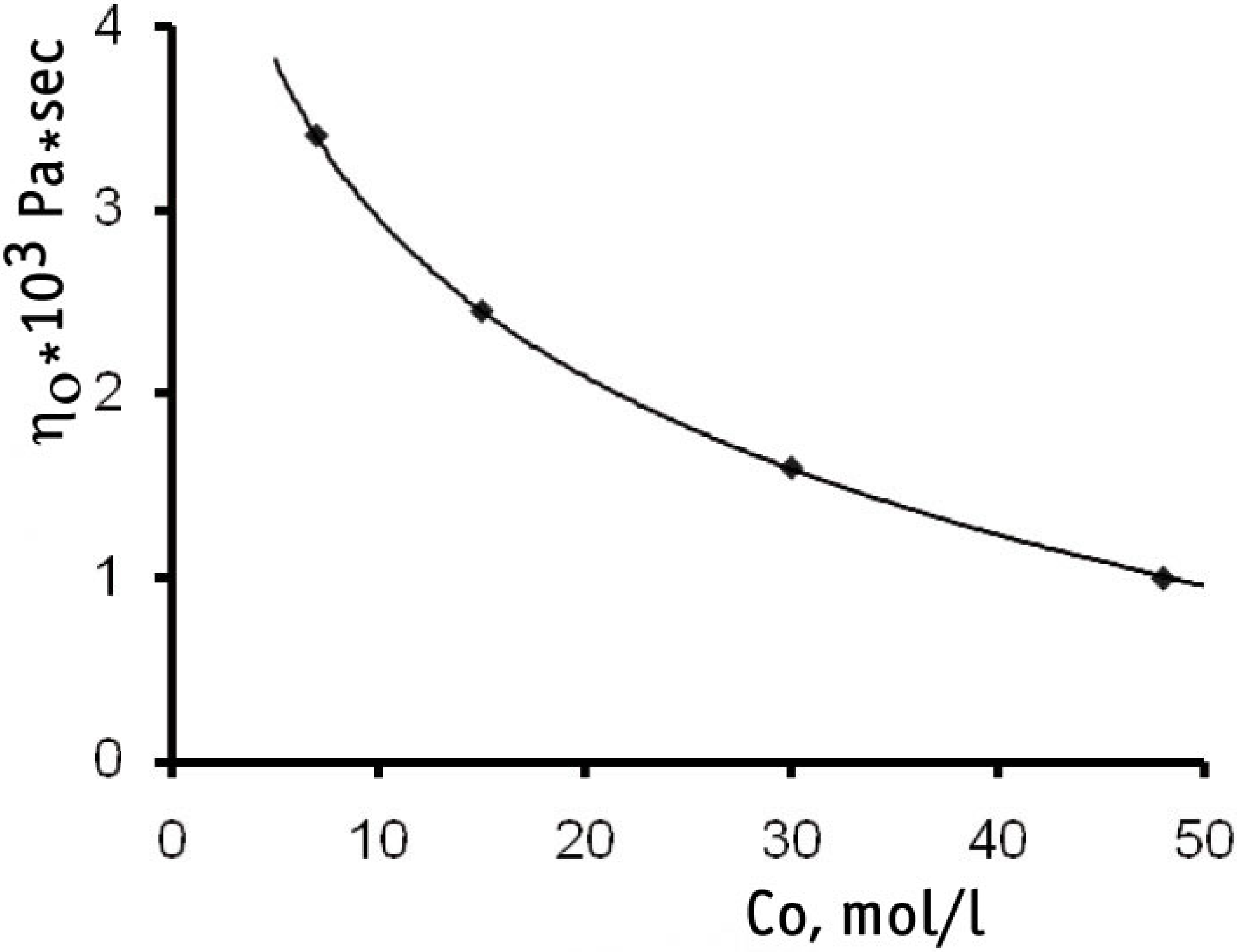


Fig. 4. *Dependence of the maximal Newtonian viscosity (η_0) of F-4CF melt co-polymer at 270^{o}C on the starting initiator concentration (Co) in the process of F-4CF co-polymer synthesis.*

Conclusions

1. In the process of radical solution TFE /FC-141 co-polymerization the increase of the initiator concentration is accompanied by:
- linear growth of the co-polymerization rate,
- decrease of the molecular weight of the produced co-polymer,
- unchanged composition (equivalent weight) of the co-polymer.

2. Order of the co-polymerization reaction by initiator is n=0.7±0.1.

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References

1. Panshin Yu. A., Malkevich S. G., Dunaevskaya C. S. Ftoroplasty. L.: Khimiya, 1978. 230s.

2. Yamabe M. Novoe v tekhnologii soedinenij ftora. M.: Mir, 1984. 521s.

3. Kirsh Yu. E., Smirnov S. A., Popkov Yu. M., Timashchev S. F.// Uspekhi khimii. 1990. t. 59. N 6. s. 970-994.

4. Waller F. G. // "Polimernye reagenty i katalizatory". M.: Khimiya, 1991. s. 46-63.

5. A. S. Odinokov, O. S. Bazanova, L. F. Sokolov, V. G. Barabanov, S. V. Timofeev.// ZhPKh, 2009. t. 82. N 1. s. 113-116.

6. Abramov S. P., Trofimova A. A., Barabanov V. G.// ZhPKh, 2009. t.82. N 12. s. 2043-2047.

7. Ryabnikova V. M., Nikolaeva A. P.// ZhAKh. 1976. t. 31. N 6. S. 1212-1214.

8. Marahonov I. A.// "Pererabotka plasticheskih mass". M.: Khimiya, 1966. s. 283.

9. Zahar'evskij M. S. Kinetika i kataliz. L.: LGU, 1963. 314 s.

10. Bagdasar'yan H. S. Teoriya radikal'noj polimerizacii. M.: Nauka, 1966. 300 s.

11. Vinogradov G. V., Malkin A. Ya. Reologiya polimerov. M.: Khimiya, 1977. 438 s.