

POLYMERIZATION OF TRIFLUOROACRYLONITRILE*

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Copolymerisation of trifluoroacrylonitrile with vinyl acetate, styrene and acrylonitrile, respectively, was studied. The values of copolymerisation parameter r_2 for the first two comonomers were found to be 0.21 and 0.67, respectively, the value of r_1 being zero. Copolymerisation parameter for acrylonitrile could not be determined because of side reactions interference. Calculated values of trifluoroacrylonitrile structural parameters Q and e are 0.057 and 3.27, respectively.

In the previous communication¹ we have found that methyl-trifluoroacrylate does not undergo homopolymerisation but easily copolymerises with vinyl acetate, styrene and vinyl chloride. Trifluoroacrylonitrile also does not homopolymerise^{2,3} and therefore we have focused our attention to the study of its copolymerisation reactions.

The copolymerisation results were evaluated analogously as in our previous study, i.e. the structural parameters Q and e were calculated from the determined values of copolymerisation parameter r_2 of two monomer couples. The copolymerisation of trifluoroacrylonitrile with a small amount of vinyl acetate has confirmed our expectation that the copolymerisation parameter r_1 is within experimental error equal to zero. Therefore, we have also in other cases assumed this parameter to be zero and restricted our study only to the region of low trifluoroacrylonitrile concentrations which is most suitable for determining r_2 values. The copolymerisation experiments with acrylonitrile in dimethylformamide solution were accompanied by side reactions which manifested themselves by the formation of yellow colour and by the evolution of a considerable amount of heat immediately after mixing of the components. Due to these unwanted reactions we were unable to determine the value of r_2 for acrylonitrile.

The results obtained (Table I) give us a certain possibility of comparing the properties of corresponding couples of fluorinated and nonfluorinated acrylic monomers. It is already known^{4,5} that fluorine atoms bonded to olefinic bond modify its chemical and physico-chemical properties. The values given in Table II indicate how the substitution of hydrogen by fluorine effects the polymerisation properties of acrylic monomers.

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The effect of substituents on the reactivity of 1,1-disubstituted ethylenes can be summarised as follows⁶: 1) Substituent electronegativity effects the value of e ; the electronegative substituents increase the value of e and the electropositive decrease it. 2) The effect of substituents on the free energy of activation is an additive one, *i.e.* each substituent effects additively the values of e and $\log Q$, furthermore, the same substituent bonded to different monomers changes these values by the same increment. However, a more detailed analysis shows⁷, that in the case of 1,1-disubstituted ethylenes the additivity rule is valid only approximatively. Even more complicated situation is with 1,2-disubstituted ethylenes. In this case no rule of the effects of substituents on the monomer reactivity⁸ can be put forward. Generally, an increasing degree of substitution leads to a lower polymerisation activity.

By comparing the two following couples of monomers – methylacrylate–methyltrifluoroacrylate and acrylonitrile–trifluoroacrylonitrile – we can see that the substitution of hydrogen by fluorine led to a lowered reactivity because none of the fluorinated monomers is able to homopolymerize at atmospheric pressure. The structural parameters were changed at the same time in the same sense as in the case of 1,1-disubstituted ethylenes: The substitution of hydrogen by fluorine at both couples of monomers made the same increase of the e value ($\Delta e = 2.06 \pm 0.01$) and the Q value decreased by a factor of about 10 ($\Delta \log Q = -0.97 \pm 0.05$).

TABLE I
Copolymerisation Parameters of Trifluoroacrylonitrile

Comonomer	r_1	r_2
Vinyl acetate	0.0	0.21 ± 0.03
Styrene	—	0.67 ± 0.1

TABLE II
Structural Parameters Q and e of Acrylic Monomers

Monomer	Q	e	References
Acrylonitrile	0.60	1.20	9
Trifluoroacrylonitrile	0.057	3.27	—
Methylacrylate	0.42	0.60	9
Methyltrifluoroacrylate	0.050	2.65	1

The effect of fluorine on the reactivity of both acrylic monomers is surprisingly identical; a somehow less satisfactory agreement with these results is found for the vinyl chloride-chlorotrifluoroethylene couple⁹, where $\Delta e = 1.12$ and $\Delta \log Q = -1.04$. This relationship is not valid for the vinylfluoride-tetrafluoroethylene couple⁹ ($\Delta e = -0.06$, $\Delta \log Q = +0.61$).

It is also interesting to note a considerably low rate of copolymerisation of trifluoroacrylonitrile with vinyl acetate, the value of it was by about two orders lower than that for the copolymerisation of methyl trifluoroacrylate. The lowered copolymerisation rate has not been observed for styrene as a parent monomer. The former observation may be either due to the presence of an impurity having a slight inhibition effect or due to a low rate constant of the reaction between vinylacetate and the radical derived from trifluoroacrylonitrile.

EXPERIMENTAL

Trifluoroacrylonitrile was prepared according to ref.¹⁰⁻¹². The preparation of other monomers, initiators and solvents is quoted in our previous communication.

Polymerisation

Trifluoroacrylonitrile was distilled under vacuum into a solution of the initiator in the comonomer. The mixture was then forced by nitrogen pressure into cooled pressure glass flasks provided with teflon closures. Copolymerisation and polymer isolation was executed according to the procedure described earlier¹. Calculation of polymer composition was based on fluorine content. Polymerisation mixture compositions: a) 25–93% mol vinyl acetate, 7–75% mol trifluoroacrylonitrile, 35 g/l dibenzoyl peroxide, 75°C, 20 h; b) 88–92% mol styrene, 8–12% mol trifluoroacrylonitrile, 6 g/l dibenzoyl peroxide, 75°C, 105 min. Conversion was about 30% wt.

Elemental analysis were performed at the section of central laboratories (Dr L. Helešic, head), Prague.

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