

POLYMERISATION OF METHYL TRIFLUOROACRYLATE*

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Copolymerisations of methyl trifluoroacrylate with vinyl acetate, styrene and vinyl chloride, respectively, were investigated. Corresponding copolymerisation parameters r_1 attain zero values for all three copolymerisations and parameters r_2 are the following: 0.24, 1.4, 1.5; average values of Q and e are 0.050 and 2.65, respectively.

Polymerisation of fluorinated acrylic acids and their derivatives has, so far, been studied very little. Copolymerisation of trifluoroacrylic acid with fluorinated olefins, perfluoro-nitroso-alkanes and with other ω -unsaturated perfluorocarboxylic acids¹ and also ternary copolymerisation of methyl trifluoroacrylate with methyl methacrylate and tetrafluoroethylene² have already been described in literature. Polymerisations of trifluoroacrylonitrile^{3,4} yielded only oligomers even if γ -rays were applied.

We have noticed that during storage of monomeric methyl trifluoroacrylate for several months in glass containers at room temperature a white precipitate, identified as homopolymer of methyl trifluoroacrylate of a low degree of polymerisation, is formed. We thought that it would be useful to investigate the possibilities of homopolymerisation and copolymerisation of this monomer at atmospheric pressure.

The results of copolymerisation experiments were evaluated according to Mayo-Lewis⁵ integrated copolymerisation equation. Analysis of copolymerisations of methyl methacrylate with styrene and vinyl acetate, respectively, and the attempts of its homopolymerisation revealed that the rate of homopolymerisation is, under the given experimental conditions, practically zero. Therefore, we have assumed that also in case of copolymerisation with vinyl chloride the value of r_1 is zero and thus the copolymerisations were carried out only in the region of low concentrations of acrylate, which are obviously the most important for the determination of the parameter r_2 . The values of r_2 for the copolymerisations with vinyl acetate, styrene and vinyl chloride are 0.24 ± 0.06 , 1.4 ± 0.2 and 1.5 ± 0.2 , respectively.

The experimentally determined copolymerisation parameters were used for the calculation of structural parameters Q and e (ref.⁶). As the values of r_1 are equal to zero, the calculation was done always with the use of the two copolymerising couples.

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This method has already been employed by Fuhrman and Mesrobian⁷ for calculating Q and e for the transfer constant of tetrabromomethane. To meet the reliability limits of the calculation it has to be observed that the difference between e_2 values of both comonomers is large enough. Otherwise, the experimental errors cause too large dispersion of calculated values of e_1 , as it follows from equation (1)

$$e_1 = e_{2a} + e_{2b} + (\ln Q_{2a}r_{2b} - \ln Q_{2b}r_{2a})/(e_{2b} - e_{2a}), \quad (1)$$

where subscript a denotes values for the first comonomer and subscript b the values for the second one. The values of Q , e for styrene, vinyl acetate and vinyl chloride have already been published⁸. The experiments of homopolymerisation of methyl trifluoroacrylate in the presence of benzoyl peroxide (60–75°C, 4–50 g/l, time 2–5 h) were not successful.

In the paper by Weis², there are also given copolymerisation parameters of methyl trifluoroacrylate with methyl methacrylate and with tetrafluoroethylene, but under different conditions (temperature 60°C, pressure 3000 atm). Under these conditions homopolymerisation of methyl trifluoroacrylate proceeds at a measurable rate and therefore the values of copolymerisation parameter r_1 differ from zero. From these copolymerisation parameters Weis has calculated also the values of Q and e for methyl trifluoroacrylate. But the numerical value of these constants does not corres-

TABLE I
Values of Q - e for Methyl Methacrylate

Exp. No	Comonomer	Q_2	e_2	Methyl trifluoroacrylate ^a	
				Q_1	e_1
1	vinyl acetate ^b	0.026	-0.22	0.063	2.24
	styrene ^b	1.0	-0.8		
2	vinyl chloride ^b	0.044	0.20	0.042	2.65
	styrene ^b	1.0	-0.8		
3	vinyl chloride ^b	0.044	0.20	0.0505	3.24
	vinyl acetate ^b	0.026	-0.22		
4	methyl methacrylate ^c	0.74	0.40	0.012 ^c	2.11 ^c
				0.38 ^d	1.50 ^d
5	tetrafluoroethylene ^c	0.049	1.22	0.196 ^c	1.50 ^c
				0.048 ^e	2.11 ^e

^a Harmonical average value of 1–3 is for Q_1 0.050, for e_1 2.65, whereas the difference between calculated and found values of r_2 is equal to one half of experimental error. ^b Ref.⁸, ^c Ref.².

^d Calculated from values² $r_1 = 0.1$, $r_2 = 3.0$. ^e Calculated from values² $r_1 = 0.15$, $r_2 = 3.0$.

pond to the value of reported copolymerisation parameters. As the author gives elsewhere in the text the same values of constants Q and e for methyl methacrylate and tetrafluoroethylene as we have used in the check calculation⁸, therefore either a misprint or a calculation error made by author is involved. To avoid confusion we shall give here the values of Q and e as they are quoted in the cited paper² and also the values calculated by us on the basis of cited copolymerisation parameters. The results are summarised in Table I.

The agreement between our results and the results published earlier is only qualitative; it is a question whether one can expect better results if the reaction conditions were so different and if the values given by Weis differ even among themselves so much.

EXPERIMENTAL

Chemicals

Methyl trifluoroacrylate was prepared according to procedures published earlier^{9,10}; prior to polymerisation it was distilled at 200 Torr; the purity was 99.7% (GLC: 20% of poly(propylene-sebacate) on Chromaton N-AW-DMCS, column: 360 cm in length and 0.6 cm in diameter, 80°C, nitrogen, flame-ionisation detection). Styrene, technical grade stabilised product (Kaučuk, Kralupy) was washed by 20% solution of sodium hydroxide, dried and prior to polymerisation it was distilled at 50 Torr; n_D^{20} 1.5461. Vinyl acetate, technical grade product (Chemical Works W. Pieck, Nováky) was rectified under pressure and stored at 0°C in a glass pressure vessel; the purity was 99.98% determined by GLC.

Tetrahydrofurane, pure (Merck, FRG), was dried by molecular sieve. Acetone, hexane and methanol were of analytical grade (Lachema, Brno). Benzoyl peroxide, pure, supplied by Argon, Poland. Isopropoxycarbonyl peroxide ("Perkadox IPP") supplied by Oxydo, FRG.

Procedure

Copolymerisation with styrene and with vinylacetate and also the experiments of homopolymerisation were performed under nitrogen in a 10 ml bulb equipped with a cooler (styrene: 75°C, benzoyl peroxide, 40–50 g/l, 1–2 h; vinyl acetate: 60°C, benzoyl peroxide 5 g/l, 5–15 min); Polymerisation was stopped by pouring the contents into a precipitant (150 ml). As a precipitant for homopolymerisation served methanol and hexane, for copolymerisation only hexane was used. Precipitated polymer was dried at 20 Torr and 70°C to constant weight. The calculation of copolymer composition was done according to fluorine content (standard analysis).

Copolymerisation with vinyl chloride was carried out in solution with exclusion of air. Glass bottles holding 20 ml equipped by metal closure and rubber and teflon sealing sheet were rotated in a thermostated bath (60°C, tetrahydrofurane 11 ml, isopropoxycarbonyl peroxide 0.2 g/l, 105 min, mixture of monomers 3.5–4.2 g). Polymerisation was stopped by cooling the contents and venting the unreacted vinyl chloride. Polymer was isolated by precipitation with methanol and drying to constant weight as it is quoted earlier.

"Spontaneous" homopolymer, which was formed during storage of methyl trifluoroacrylate in glass vessels, was purified by digestion with acetone and by evaporation of the solvent. Calculated $(C_4H_3F_3O_2)_n$ (140.1): 34.40% C, 2.16% H, 40.61% F; found: 33.38% C, 2.42% H, 36.27% F; molecular weight 1280 (Vapour Phase Osmometry, acetone).

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