Suspension copolymerization of vinyl chloride with vinyl acetate initiated by diisopropyl peroxydicarbonate formed *in situ*

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Dedicated to Professor Dr. Ing. M. Marko, in honour of his 75th birthday

The kinetics of suspension copolymerization of vinyl chloride (VC) with vinyl acetate (VAC) initiated by diisopropyl peroxydicarbonate formed *in situ* or outside the medium of copolymerization (or in the absence of VAC) as well as by commercial preparation have been studied. In all cases, the reaction course is governed by a kinetic equation of the first-order reaction. But the rate of copolymerization with the initiator prepared beforehand (in the absence of VAC) or a commercial initiator is more than five times greater than the rate with the initiator prepared *in situ*. The cause consists mainly in simultaneous consumption of sodium hydroxide for the neutralization of acetic acid and, in particular, saponification of VAC. The kinetics of synthesis of the above initiator as well as mixed initiators show that the reaction time of 20 min is sufficient to obtain a yield of 85—90% at temperatures varying in the range 5—20°C. Afterwards, not only VC but also VAC may be added and copolymerization successfully performed.

Изучена кинетика сополимеризации в суспензиях винилхлорида (ВХ) и винилацетата (ВАЦ), которая была инициирована диизопропилпероксидикарбонатом, образующимся прямо в сополимеризационной среде или вне ее и также с комерческим продуктом или в отсутствии ВАЦ. Для всех случаев пригодно уравнение 1-го порядка. Скорость сополимеризации, однако, в случае заранее приготовленного или комерческого инициатора (в отсутствии ВАЦ) в пять раз выше, чем в случае его образования в системе. Причиной этого является в основном одновременный расход гидроокиси натрия на нейтрализацию уксусной кислоты и особенно на омыление ВАЦ. Из кинетики синтеза вытекает, что при температуре водной фазы 5—20°C достаточно реакционное время 20 мин для выхода 85—90%. После этого времени можно добавить не только ВХ, но и ВАЦ и успешно осуществить сополимеризацию.

The suspension homopolymerization and copolymerization of vinyl chloride initiated by dialkyl peroxydicarbonates formed *in situ* from the starting raw materials attracted attention already earlier [1—7]. Though the study of initiators

formed *in situ* [8, 9] continues incessantly, these initiating systems have not yet been of technical use for several reasons. It is, therefore, important to find out the conditions of formation of such initiating systems, explain some apparent anomalies and clear up the possibility of formation of the initiators *in situ* in the medium of suspension copolymerization of vinyl chloride with vinyl acetate. Moreover, we investigated the kinetics of synthesis of diisopropyl peroxydicarbonate itself, dibenzoyl peroxide, and mixed peroxide.

Experimental

Chemicals

VC (product of W. Pieck Chemical Works, Nováky) nonstabilized contained the following admixtures (in mass %): acetylene 5×10^{-4}, vinyl bromide 1.1×10^{-4}, 1,1-dichloroethylene 6.8×10^{-3}, 1,1-dichloroethane 1.7×10^{-3}, methanol 7.9×10^{-3}, *cis*-1,2-dichloroethylene and other impurities.

VAC rectified in nitrogen atmosphere in a column with 14 TP and a reflux ratio 1 : 15; fraction with b.p. = 71.9—72°C/100.8 kPa, $\varrho_{20°C} = 932.9$ kg m^{-3}, $n_D^{20} = 1.3968$, acid number 0.35 mg KOH/g.

Isopropyl chloroformate, b.p. = 101—102.5°C/100.6 kPa, $\varrho_{20°C} = 1071$ kg m^{-3}, $n_D^{20} = 1.3996$, content of the main component 85 mass %.

Hydrogen peroxide (Lachema, Brno) of 30 mass % concentration. The aqueous solution used was of 4 mass % concentration. The accurate composition of the aqueous solution of hydrogen peroxide was determined in three-day intervals.

Sodium hydroxide of 98.9 mass % purity. The experiments were carried out with the aqueous solution of 24.2 mass % concentration.

The concentration of diisopropyl peroxydicarbonate in toluene was 29.12 mass %. It was stored at $-10°C$ and the content of active oxygen was 2.26 mass %.

Methyl hydroxypropyl cellulose (Metocel 65 HG). Content of methoxy groups 28 mass % and hydroxypropyloxy groups 6.3 mass %. It was applied in the form of aqueous solution of 0.2 mass % concentration.

Working procedures

The kinetics of suspension copolymerization of VC with VAC initiated by the effect of diisopropyl peroxydicarbonate formed from the starting raw materials *in situ* were investigated in glass thick-walled tubes of the volume of 100 cm³. We put 40 g of the aqueous solution of methyl hydroxypropyl cellulose (0.2 mass % concentration), the necessary amount of hydrogen peroxide, aqueous solution of sodium hydroxide, isopropyl chloroformate, and 5 g of VAC into each tube. Afterwards we removed air and added 15 g of VC. The tubes were attached to a rotating shaft (36 revolutions per min) and dipped into a temperature-controlled bath. The temperature of this bath was controlled with accuracy ±0.5°C. The individual tubes were taken in required time intervals, rapidly cooled by dipping into cold water, and degasified. Then the total content of tubes was filtered, the

suspension of copolymer was washed three-times with warm distilled water and dried under reduced pressure at 60°C. The amount of the obtained copolymer was used for calculating its yield.

The kinetics of the copolymerization initiated by diisopropyl peroxydicarbonate prepared outside the copolymerization medium were so investigated that 20 g of the aqueous solution of methyl hydroxypropyl cellulose (0.4 mass % concentration) was put into Erlenmeyer flasks and subsequently the calculated quantities of hydrogen peroxide, sodium hydroxide, and isopropyl chloroformate were added under constant stirring. After 40 min intensive stirring the content of Erlenmeyer flasks was poured into thick-walled tubes and the residue was washed with further 20 g of distilled water. Then VAC and VC were added into the tubes and the copolymerization was performed as already described.

The rate constants were calculated from kinetic equations by means of a desk computer Hewlett—Packard 9100 B.

The time of inhibition t_0 was determined from the equation of regression straight line. We assumed that the overall time of copolymerization t' was equal to the value of the time of inhibition provided log $a/(a - x) = 0$ (a — initial concentration of monomers, x — decrease in the monomers concentration in the time t).
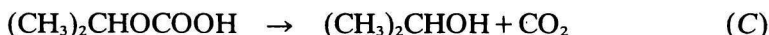
The organic peroxides were determined according to *Mair* and *Graupner* [10], the only difference being that the temperature was reduced to 70—80°C and the reaction time extended from 5 to 20 min.

Results and discussion

The influence of temperature in the range 38—60°C on kinetics of the copolymerization of VC with VAC was measured in systems with 0.5 mass % (referred to monomers) of the expected initiator formed *in situ* from the starting raw materials (0.118 g isopropyl chloroformate, 0.43 g H_2O_2 of 3.83 mass % concentration, and 0.159 g NaOH of 24.2 mass % concentration) according to the following equation

$$2(CH_3)_2CHOCOCl + H_2O_2 + 2NaOH \rightarrow$$
$$\rightarrow (CH_3)_2CHOCO—O—O—COOCH(CH_3)_2 + 2NaCl + 2H_2O \qquad (A)$$
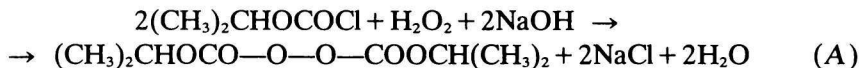
We also took into account the subsequent possible simultaneous reactions

$$(CH_3)_2CHOCOCl + H_2O \rightarrow (CH_3)_2CHOCOOH + HCl \qquad (B)$$

$$(CH_3)_2CHOCOOH \rightarrow (CH_3)_2CHOH + CO_2 \qquad (C)$$

The course of the copolymerization experiments carried out in the temperature range 52—60°C is graphically represented in Fig. 1.

Because of possible occurrence of reactions (B) and (C), we allege the maximum possible 0.5% (by mass) concentration of diisopropyl peroxydicarbonate formed from the above starting raw materials.
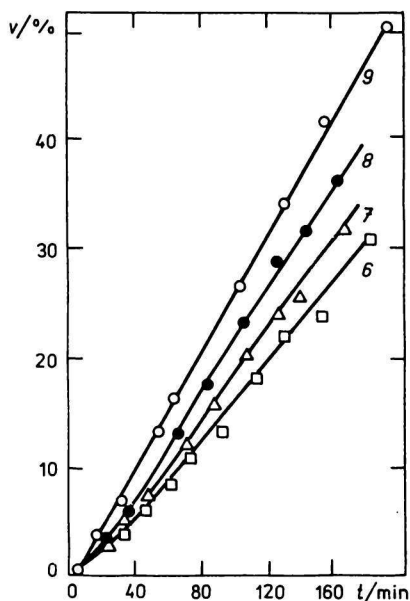
Fig. 1. Influence of temperature on kinetics of copolymerization of VC with VAC in the presence of max. 0.5 mass % of diisopropyl peroxydicarbonate formed *in situ* (v/% yield of copolymer).
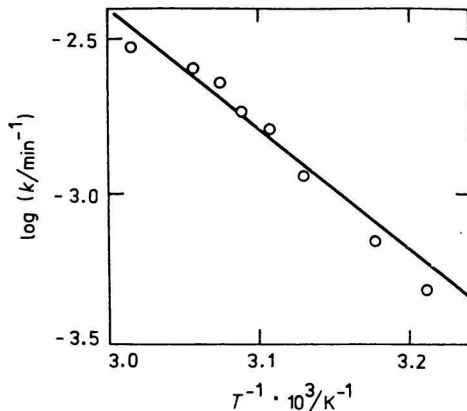6. 52°C; 7. 54°C; 8. 58°C; 9. 60°C.

Fig. 2. Logarithm of the rate constant k/min^{-1} of kinetic equation of copolymerization of VC with VAC as a function of the reciprocal value of absolute temperature. Max. 0.5 mass % concentration of diisopropyl peroxydicarbonate formed *in situ*.

Since the course of copolymerization under described conditions was governed by the kinetic equation of the first-order reactions, we subjected the experimental data of all experiments to regression analysis. Fig. 2 represents the logarithm of the rate constant k/min^{-1} as a function of reciprocal value of the absolute temperature T (K).

Then the following equation expresses the dependence of the rate constant k/min^{-1} on temperature

$$\log k/\text{min}^{-1} = (9.779 \pm 1.048) - (4053.5 \pm 338.7) \, T^{-1}/\text{K}^{-1}$$

The values of activation energy E, standard deviation of the measured values about the regression straight line S_{xy}, and coefficient of correlation of the linear regression r_{xy} ($x = \text{K}/T$ and $y = \log k/\text{min}^{-1}$) are $E = 77.6 \pm 6.5 \text{ kJ mol}^{-1}$, $S_{xy} = 0.0666$, and $r_{xy} = -0.9693$, respectively.

Fig. 2 documents the relatively good linear relationship $\log k/\text{min}^{-1} = f(\text{K}/T)$ which was also confirmed by the low value of standard deviation of the measured values and high value of the coefficient of correlation of linear regression. The

value of activation energy does not substantially differ from the values corresponding to analogous radical homopolymerizations and copolymerizations of monomers. The evaluation of the measured and calculated data obtained for copolymerization shows that we achieved relatively low reaction rates or rather low yields of copolymer even for quite long times of copolymerization in comparison with the known data obtained [11] for copolymerization with separately prepared peroxidic initiators or with the data obtained for homopolymerization of VC with initiators formed *in situ* [2, 3, 7]. For comparison, we carried out copolymerization at 50 ± 0.1°C with 0.25 mass % and 0.5 mass % of diisopropyl peroxydicarbonate formed *in situ* and formed outside the medium of copolymerization (or in the absence of VAC) as well as with commercial preparation. The results were reproducible and were not significantly affected by the errors of the procedure and analytical methods. The comparison of the courses of copolymerizations is graphically represented in Fig. 3.

These results show that the conversion of monomers achieved with an initiator formed outside the medium of copolymerization (in the absence of VAC) as well as
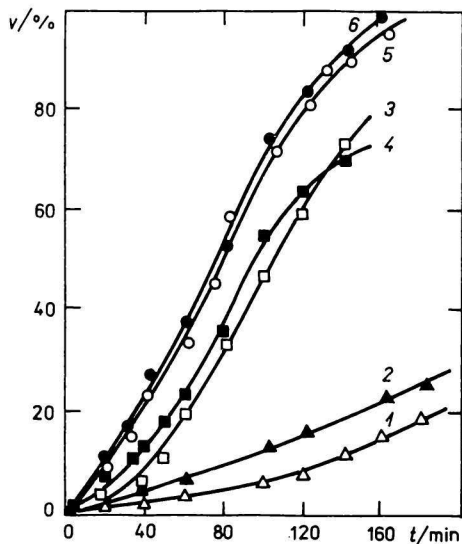

Fig. 3. Copolymerization of VC with VAC in the presence of 0.25 and 0.50 mass % of diisopropyl peroxydicarbonate at 50 ± 0.1°C (v/% yield of copolymer).

1, 2. Initiator formed *in situ* (1. with 0.25 mass % of initiator); 3, 5. initiator formed outside the copolymerization medium; 4, 6. commercial initiator (4. with 0.25 mass % and 6. with 0.50 mass % of initiator).
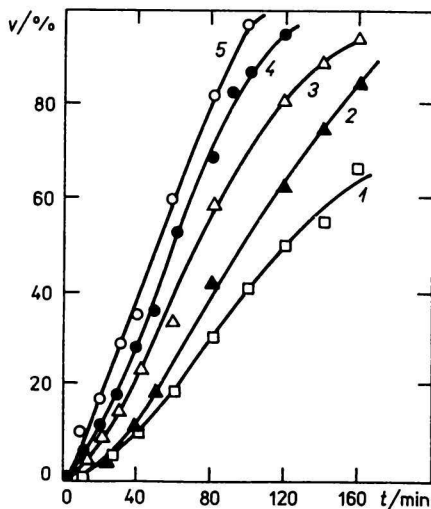
Fig. 4. Influence of temperature on the course of copolymerization of VC with VAC in the presence of 0.5 mass % of diisopropyl peroxydicarbonate formed from the starting raw materials in the absence of VAC (v/% yield of copolymer).

1. 43°C; 2. 46°C; 3. 50°C; 4. 56°C; 5. 58°C.

with commercial diisopropyl peroxydicarbonate is almost five times greater than that obtained with an initiator formed *in situ*. These great differences are due not only to the competing hydrolysis of isopropyl chloroformate according to eqns (B) and (C) but also to the hydrolysis of vinyl acetate according to the following equations

$$CH_2{=}CHOCOCH_3 + H_2O \xrightarrow{\text{OH}^-} [CH_2{=}CHOH] + CH_3COOH \qquad (D)$$
$$\downarrow$$
$$CH_3CHO \qquad\qquad\qquad\qquad (E)$$

$$CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O \qquad (F)$$

This hydrolysis involves a consumption of sodium hydroxide which is thus lacking in the synthesis of diisopropyl peroxydicarbonate *in situ* according to eqn (A).

In order to verify this assumption, we tried to subject VAC to hydrolysis in the presence of sodium hydroxide under intensive stirring and equal conditions as used for copolymerization. We observed the time in which the used amount of VAC with an admixture of phenolphthalein as indicator consumed all sodium hydroxide added. Moreover, we chromatographically determined acetaldehyde in the products. All experimental conditions and the results obtained are summarized in Table 1.

Table 1

Influence of temperature and intensive stirring on time of consumption of the added sodium hydroxide in the presence of VAC

Solvent		NaOH g	VAC g	Temperature °C	Time of consumption of NaOH s
Kind	Quantity g				
Distilled water	40	0.0384	40	22	65
Aqueous solution of methyl hydroxypropyl cellulose of 0.2 mass % concentration	20	0.0192	10	27	45
Aqueous solution of methyl hydroxypropyl cellulose of 0.2 mass % concentration	20	0.0192	10	31	40
Aqueous solution of methyl hydroxypropyl cellulose of 0.2 mass % concentration + 0.0082 g of hydrogen peroxide	20	0.0192	10	27	45
—	0	0.384	20	34	135
—	0	0.384	20	37	75

It ensues from these results that sodium hydroxide is very rapidly consumed not only by VAC in distilled water but also by VAC itself. This consumption is still more rapid in the presence of dispersing agents. That is comprehensible because the dispersing agent (protective colloid) improves the contact of the organic phase (VAC) with water. Therefore we investigated the concentration increase of acetic acid in the reaction solution at $50 \pm 0.1°C$ by means of a particular experiment (80 g of aqueous solution of methyl hydroxypropyl cellulose of 0.2 mass % concentration and 40 g of VAC). The concentration of acetic acid increased in the course of 300 min from original 0.0022 mass % to 0.07 mass %.

Furthermore, we carried out a series of experiments by using diisopropyl peroxydicarbonate prepared outside the copolymerization medium (especially in the absence of VAC). The influence of temperature on the copolymerization of VC with VAC is represented in Fig. 4 for the constant maximum amount (0.5 mass %) of initiator formed in the absence of VAC.

The course of copolymerization also follows a kinetic equation of the first-order reaction in this case. Then the relationship between the rate constant k_h and temperature for the constant 0.50 mass % concentration of diisopropyl peroxy-dicarbonate can be expressed by the equation

$$\log k_h/min^{-1} = (11.9302 \pm 1.5298) - (4419.95 \pm 494.97)\ T^{-1}/K^{-1}$$

the activation energy being $E_h = 84.6 \pm 9.5$ kJ mol^{-1}. If the constant concentration of initiator is 0.25 mass %, it holds

$$\log k_h/min^{-1} = (13.405 \pm 1.610) - (4941.65 \pm 522.66)\ T^{-1}/K^{-1}$$

and the activation energy is $E_h = 94.6 \pm 10.0$ kJ mol^{-1}.

The results obtained with the initiator prepared outside the copolymerization system make evident that the rate constants not only increase with temperature but also are almost by one decimal order greater in contrast to the results obtained with the initiators formed *in situ*.

The data concerning the hydrolysis of VAC and isopropyl chloroformate stimulated us to investigate the kinetics of synthesis of diisopropyl peroxydicarbo-nate (0.2 M) in toluene solution at varying temperature (Fig. 5). It may be deduced from the plots in Fig. 5 that the reaction time necessary for the formation of diisopropyl peroxydicarbonate *in situ* in PVC factory production is 10—30 min provided the water temperatures used for suspension copolymerization of VC with VAC are in the range 0—20°C. The time period of 10 min is sufficient at 30°C while the peroxide formed evidently decays at temperatures above 40°C.

The temperature dependence of the rate constant k_{DIPD} of the formation of diisopropyl peroxydicarbonate from the starting materials is governed within the
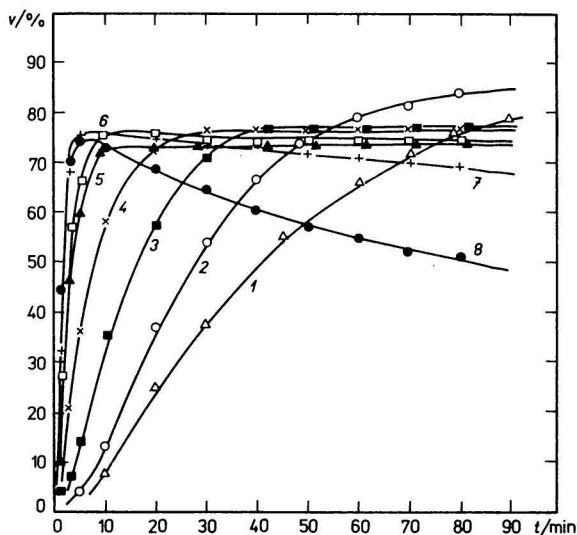
Fig. 5. Kinetics of synthesis of diisopropyl peroxydicarbonate (0.2 M) in toluene solution at varying temperature (v/% yield of copolymer).
1. − 20°C; *2.* − 10°C; *3.* 0°C; *4.* 20°C; *5.* 30°C; *6.* 40°C; *7.* 50°C; *8.* 60°C.

temperature range 250—340 K by the following equation

$$\log k_{DIPD}/min^{-1} = 5.022 \pm 0.200) - (1696.1 \pm 58.2) \, T^{-1}/K^{-1}$$

and the activation energy is $E_{DIPD} = 14.1 \pm 0.5 \text{ kJ mol}^{-1}$.
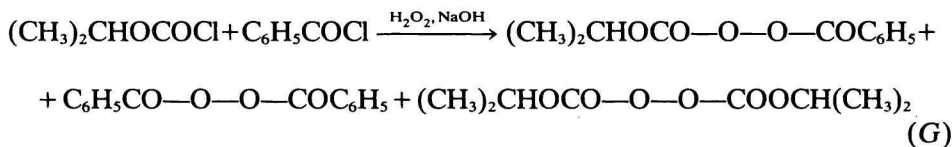
Similarly, the kinetics of synthesis of dibenzoyl peroxide from benzoyl chloride, hydrogen peroxide, and sodium hydroxide in the temperature range 250—300 K obey the kinetics equation

$$\log k_{DBP}/min^{-1} = (3.878 \pm 0.362) - (1221.5 \pm 104.8) \, T^{-1}/K^{-1}$$

the activation energy being $E_{DBP} = 10.2 \pm 0.9 \text{ kJ mol}^{-1}$.

Thus in order to obtain dibenzoyl peroxide (Fig. 6) in the yield of 92—95%, the reaction time of 5—15 min is sufficient in the temperature interval 0—20°C.

The kinetics of formation of a mixture of peroxides or mixed peroxides from isopropyl chloroformate and benzoyl chloride (mol 1 : 1 ; 0.24 M) according to the following reaction scheme

$$(CH_3)_2CHOCOCl + C_6H_5COCl \xrightarrow{H_2O_2, NaOH} (CH_3)_2CHOCO—O—O—COC_6H_5 +$$

$$+ C_6H_5CO—O—O—COC_6H_5 + (CH_3)_2CHOCO—O—O—COOCH(CH_3)_2$$
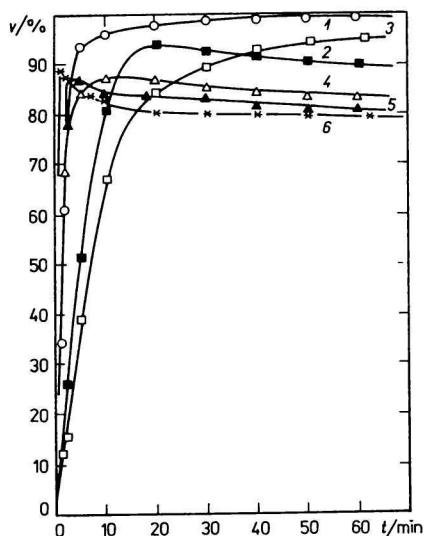
$$(G)$$

are represented in Fig. 7.

Fig. 6. Kinetics of synthesis of dibenzoyl peroxide from benzoyl chloride, hydrogen peroxide, and 0.2 M sodium hydroxide in toluene at varying temperature (v/% yield of copolymer). 1. 20°C; 2. −5°C; 3. −20°C; 4. 30°C; 5. 40°C; 6. 50°C.
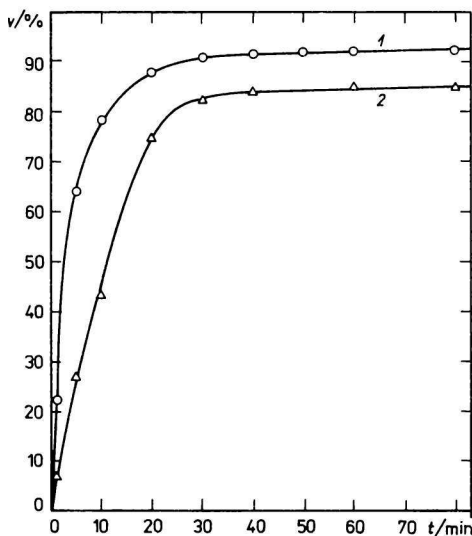
Fig. 7. Kinetics of synthesis of mixed peroxide from a mixture of isopropyl chloroformate and benzoyl chloride (1:1 mol/mol, 0.24 M solution) in toluene (v/% yield of copolymer). 1. 20°C; 2. −5°C.

Then we carried out a series of measurements so that we added hydrogen peroxide, sodium hydroxide, and isopropyl chloroformate under stirring at room temperature into the flasks with the aqueous phase and 20 min after adding isopropyl chloroformate we put VAC in. Subsequently, we closed the flasks, removed air, and added vinyl chloride. The results were comparable with the preceding results obtained with the initiator solutions prepared outside the medium of copolymerization. In a similar way, we determined the influence of the amount of initiator (diisopropyl peroxydicarbonate) at the temperature $50 \pm 0.1°C$ (Fig. 8). The variation of the rate constant k_h/min^{-1} of kinetic equation with concentration of the initiator c (mass % referred to monomers) at $50 \pm 0.1°C$ is represented in Fig. 9.

The results are in agreement with the results obtained by the use of the initiator prepared in a separate vessel and almost correspond to the results obtained with commercial diisopropyl peroxydicarbonate (the efficiency is 0.9, which is consistent with 90% yields of initiator).

The correctness of these results was corroborated by the experiments in pilot plant and in manufacture scale [7]. The experiments in pilot plant scale were so performed that, first of all, the starting components of the initiation system and
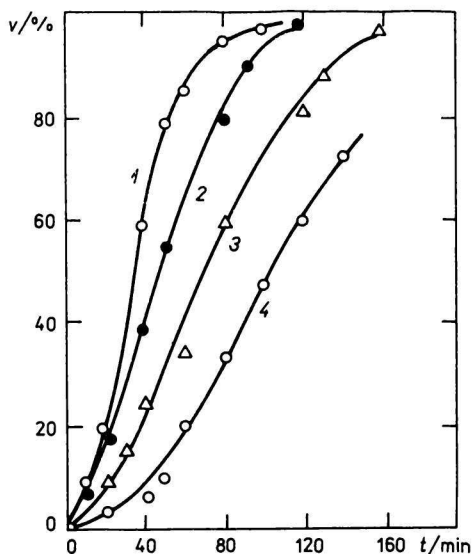
Fig. 8. Kinetics of suspension copolymerization of VC with VAC at varying concentration of the initiator formed outside the copolymerization medium at 50 ± 0.1°C (v/% yield of copolymer).

1. 1.0 mass %/VC + VAC; *2.* 0.875 mass %/ /VC + VAC; *3.* 0.50 mass %/VC + VAC; *4.* 0.25 mass %/VC + VAC.
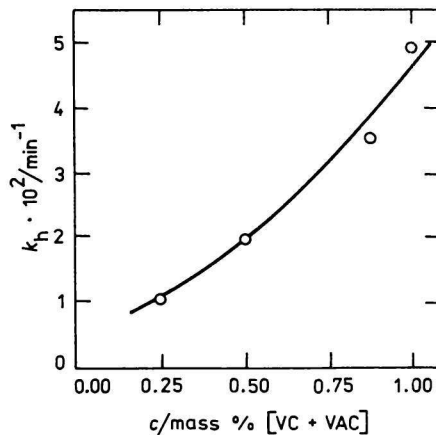
Fig. 9. Variation of the rate constant of copolymerization of VC with VAC with concentration of the initiator formed outside the copolymerization medium at 50 ± 0.1°C.

subsequently in the period of time 10—25 min VAC and VC were added into the aqueous phase containing methyl hydroxypropyl cellulose and other components. In this way, we could achieve the reaction rates of copolymerization corresponding to the yield or amount of initiator attaining 85—90% of the theoretical value.

Conclusion

We have shown that it is not suited to carry out the suspension copolymerization of VC with VAC by means of an initiation system formed *in situ* in the presence of VAC because of the consumption of sodium hydroxide for the reaction with acetic acid and saponification of VAC. On the other hand, if the initiation system is formed during 10—25 min in an autoclave before the addition of VAC (it is also valid for mixed initiators and initiator mixtures), the reaction rate is near to the rate with diisopropyl peroxydicarbonate prepared beforehand or corresponds to 85—90% effectiveness of a commercial initiator. A similar situation is in case of other acid monomers, comonomers or other acid admixtures given into the medium of homopolymerization or copolymerization of VC.

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References

1. Smith, E. S., *U.S.* 3022281 (1961).
2. Macho, V., Porubský, J., Kordík, J., and Polievka, M., *Czech.* 149822 (1973); notified 23 April 1971.
3. Macho, V., Porubský, J., Kordík, J., Polievka, M., and Jarošek, K., *Czech.* 155868 (1974); notified 23 April 1971.
4. Benton, J. L., *Brit.* 1262706 (1972).
5. Macho, V., Porubský, J., Kordík, J., Rusina, M., and Volek, D., *Czech.* 169966 (1977); notified 12 December 1972.
6. Barter, J. A., *U.S.* 3923766 (1975).
7. Macho, V., Rusina, M., Porubský, J., and Kohút, A., *Czech.* 175738 (1976).
8. Ravey, M. and Waterman, J. A., *J. Polym. Sci. 15*, 2521 (1977).
9. Ravey, M., *J. Polym. Sci. 15*, 2559 (1977).
10. Mair, R. D. and Graupner, A. J., *Anal. Chem. 36*, 194 (1964).
11. Emmer, E. J. and Bankhoff, S. G., *Ind. Eng. Chem. 46*, 637 (1954).

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