Kinetics of the vinyl chloride—vinyl acetate copolymer dissolution in cyclohexanone

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The kinetics of the vinyl chloride—vinyl acetate copolymer dissolution in cyclohexanone was studied. The values of the induction periods t_Q and the rates of dissolution u_{OC} are presented. The kinetic study was performed with four samples. The composition of copolymers was determined by chromatographic analysis of the gaseous products after the pyrolysis of samples (650°C). It has been found that the values of activation parameters corresponding to the diffusion dissolving process vary with temperature in the interval between 10 and 40°C which indicates a low value of T_g occurring in this temperature range.

The rate of the dissolution of macromolecular substances was controlled by several processes. First of all, it was determined by the rate of the diffusion of liquid solvent into the solid polymer sample. The process of dissolution itself most frequently proceeds at temperatures below T_g only after a certain induction period of diffusion dissolving process has elapsed and it shows a stationary character under defined hydrodynamic conditions. The thickness of a swollen surface layer formed in the course of the induction period does not change during the period of stationary isothermal dissolution. The diffusion process involving the dissolution of macromolecular substances is characterized by the following kinetic parameters: mean mutual diffusion coefficient $\bar{D}$, the temporal retardation of the proper process of dissolution t_Q, the rate of dissolution u_{OC} (defined as the rate of the movement of optical phase boundary to the centre of sample), the activation energies corresponding to the diffusion process of swelling E_s and dissolution E_d.

The values of these parameters are functions of temperature, pressure, hydrodynamic conditions, and the degree of arrangement of the solid polymer phase.

The aim of this study is to evaluate the effect of chemical heterogeneity of polymer chain on the kinetic parameters of diffusion dissolving process.

The relative proportion of the components of copolymer was estimated according to the content of methane, acetylene, and vinyl acetate in the gaseous products of the sample pyrolysis performed in a nitrogen stream at 650°C. The quantitative analysis of the products obtained by the pyrolysis of VC—VAc copolymers and corresponding homopolymers was studied by many investigators [1—5], who stated that a calibration by means of various copolymer standards was not necessary for the system studied because the calibration with individual homopolymers answered the purpose.

Experimental

Cyclohexanone

Cyclohexanone, anal. grade (Lachema, Brno) was carefully rectified on a column at atmospheric pressure. Its purity was checked by measuring the refractive index on an Abbé refractometer (Zeiss, Jena). The refractive index of the fractions used varied in the range from 1.45090 to 1.45100 which is in good agreement with the data reported in literature [6] (t = 20.00°C).

Copolymer vinyl chloride—vinyl acetate

The following samples of copolymer were studied:

1. copolymer prepared by the copolymerization of monomers in suspension;
2. copolymer prepared by the copolymerization in the form of latex;
3. copolymer prepared by the copolymerization in solution;
4. standard sample of the copolymer of American provenance (Du Pont).

The samples of the studied copolymers had the following approximate characteristics: $M = 5 \times 10^5$, $T_g = 45°C$.

Pyrolysis of copolymers

A pyrolyzer of reactor type described in paper [7] was used. The pyrolyzer is based on the sample decomposition in a molten tin bath kept at a constant temperature (650°C)

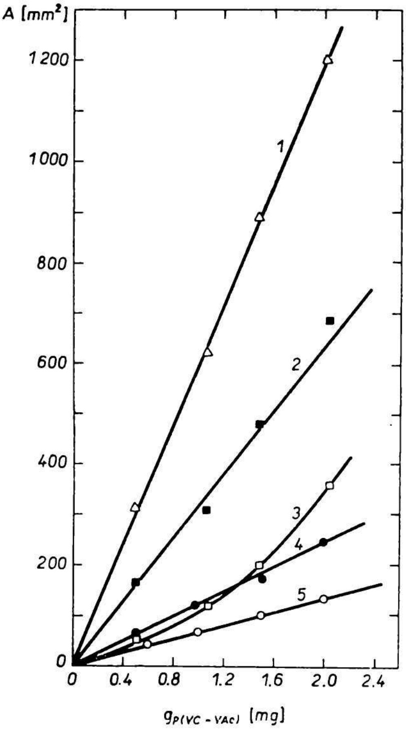


Fig. 1. Calibration graph: *1.* methane from PVAc; *2.* acetylene from PVAc; *3.* vinyl acetate from PVAc; *4.* methane from PVC; *5.* acetylene from PVC. Pyrolysis temperature 650°C.

accurate to ±10°C. The sample was weighed into tin capsules which were put into the tin bath by means of a solenoid. A constant flow of the carrier gas (N_2, 25 ml/min) was passed through a quartz flask of the tin bath. The gaseous products were supplied into a Hewlett—Packard 5750 gas chromatograph with a flame ionization detector and a column (1.8 m × 2.2 mm) packed with Chromosorb W (graining 0.147—0.175 mm) on which 10 weight % of the silicone polymer UCCW 982 were laid. The temperature of column was maintained at 25°C for 8 min and subsequently raised linearly with time (10°C/min) up to 270°C.

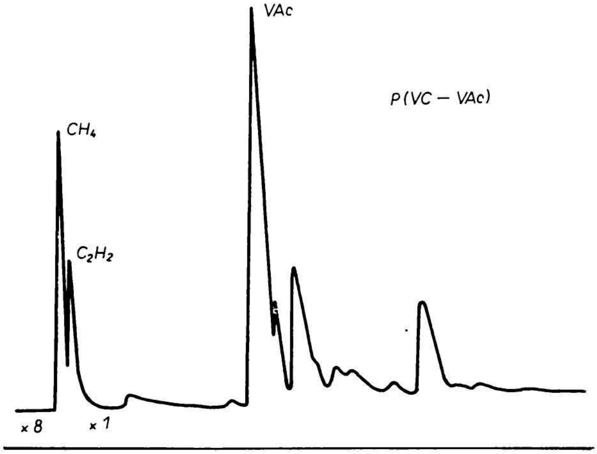


Fig. 2. Chromatogram of the pyrolysis products from VC—VAc copolymer.

The temperature of 650°C of pyrolysis was chosen purposely in order to prevent an excessive formation of hydrogen chloride which damages the column and detector. The identification of chromatographic waves was performed merely for methane, acetylene, and vinyl acetate which were also used for calibration (Fig. 1). From the calibration curve it is obvious that the amounts of methane and acetylene produced by the thermal

Table 1

Composition of the copolymer vinyl chloride—vinyl acetate in weight % of vinyl chloride

Sample	According to the content of CH_4	 C_2H_2 in gaseous pyrolysis products	 VAc	Average value
1	81.0	80.5	82.7	81.4
2	96.3	94.5	93.5	94.8
3	76.4	76.1	76.2	76.2
4	56.0	47.5	48.3	47.9

decomposition of PVAc are approximately three times greater than those produced by the thermal decomposition of PVC under the same conditions. The chromatogram of the pyrolysis products of the copolymer VC—VAc is presented in Fig. 2. Results of the estimation of the copolymer components are given in Table 1.

Preparation of solid polymer film

The samples in the form of films (thickness about 0.8 mm) were prepared by pouring a 1% solution of the polymer in dichloroethane on a glass plate. The solid polymer film was carefully deprived of the solvent residues by suction in a vacuum drier at 1 torr. This procedure lasted several weeks.

Apparatus for kinetic measurements

The experimental equipment is based on the determination of the concentration of the sample dissolved in the liquid phase by measuring the refractive index at different times. A detailed description of the equipment can be found in the preceding paper [8].

Results and discussion

The kinetic curves expresseing the dissolution of the samples of VC—VAc copolymer in cyclohexanone (Fig. 3) do not differ from the kinetic curves of both non-fractionated and fractionated samples of PVC [8, 9]. They exhibit a characteristic induction period, t_Q, which is considerably shorter than that obtained with a non-fractionated PVC sample of equal molecular weight [9].

In the course of kinetic measurements no disintegration of smooth kinetic curves was observed in the region of lower temperatures in contrast to the results obtained with PVC homopolymer [10]. It may be assumed that the linking of vinyl acetate units

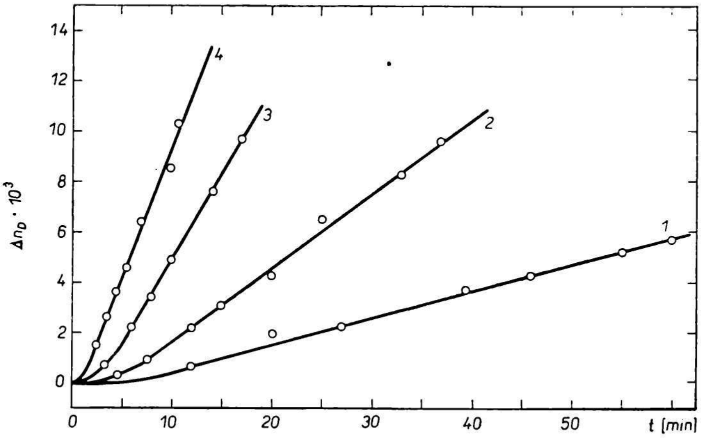
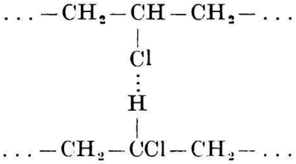


Fig. 3. Kinetic curves for the dissolution of VC—VAc copolymer in cyclohexanone (sample *1*).
Temperatures: *1.* 10°C; *2.* 20°C; *3.* 30°C; *4.* 40°C.

in a polymer chain of PVC interferes with the formation of strong hydrogen bonds of the type



$$\begin{array}{c}\ldots-CH_2-CH-CH_2-\ldots\\ |\\ Cl\\ \vdots\\ H\\ |\\ \ldots-CH_2-CCl-CH_2-\ldots\end{array}$$

Furthermore, owing to a great volume of the acetate groups when compared with the volume of chlorine atom, this group reduces the intensity of the Coulomb interactions between neighbouring chains as well as inside a chain. The degree of packing of individual polymer coils is smaller which is also confirmed by lower values of the densities of solid copolymers in comparison with a PVC homopolymer. The values of the induction periods of diffusion dissolving process, t_Q, as a function of time are given for individual samples in Fig. 4. As obvious from Fig. 4 the value of the effective activation energy

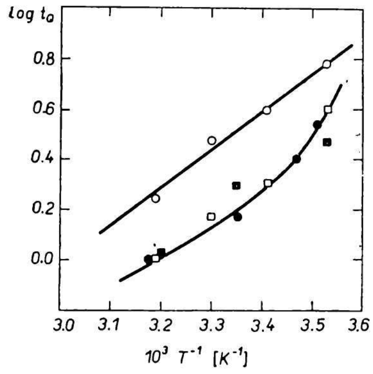


Fig. 4. Induction period as a function of temperature for the diffusion process of the dissolution of VC—VAc copolymer in cyclohexanone.
○ 94.8% VC; □ 81.4% VC; ■ 76.2% VC; ● 47.9% VC.

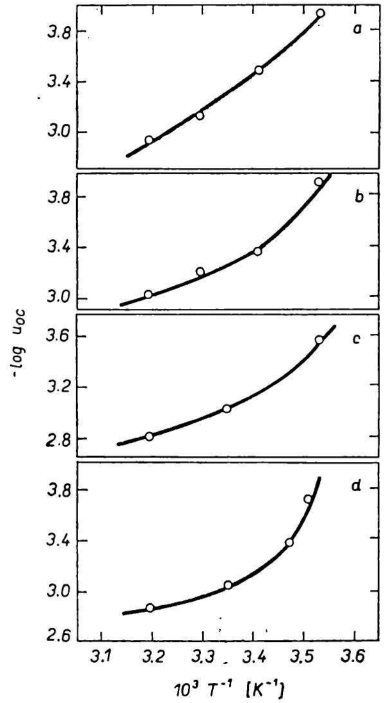


Fig. 5. The rate of the dissolution of VC—VAc copolymer in cyclohexanone as a function of temperature.
a) 94.8% VC; *b*) 81.4% VC; *c*) 76.2% VC; *d*) 47.9% VC.

of diffusion swelling process defined by eqn (*1*) decreases with the increasing temperature [11]. Sample *2* represents an exception which may be explained by the relatively highest degree of chemical homogeneity (94.8% VC).

$$[E_\mathrm{s}]_\mathrm{P} = RT^2 \left[\frac{\partial \ln t_2}{\partial\left(\dfrac{1}{T}\right)}\right]_\mathrm{P} \cdot \qquad (1)$$

According to [12] the second-order transition point manifests itself on the straight lines $\ln u_\mathrm{OC} = \mathrm{f}(1/T)$ by a sharp break which cannot be observed in the case of the copolymers studied (Fig. 5). It seems that for a copolymer VC—VAc the transition from one dissolving mechanism (at $T < T_\mathrm{g}$) to another (at $T > T_\mathrm{g}$) takes place in a wider temperature interval because of a greater structural variability. From the results of the kinetic measurements it is evident that for this copolymer as well as for a PVC homopolymer the kinetic dissolving process is controlled by the diffusion of solvent.

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