Copolymerization of Vinyl Chloride with 1-Olefins. III. An Investigation of the Copolymerization Reaction of Vinyl Chloride with 1-Butene and 1-Pentene

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Synopsis

Series of suspension copolymerizations of vinyl chloride with various contents of 1-butene and 1-pentene (5–30 mass%) were carried out under the same reaction conditions. By applying a method which utilizes periodic sampling of heterogeneous reaction mixture from the reactor during the reaction and a gas chromatographic determination of unreacted vinyl chloride in the sample, the conversion curves of vinyl chloride were determined and the initial reaction rates were compared.

INTRODUCTION

In our earlier paper[1] we described a new method of investigation of the reaction course of the polymerization and copolymerization of vinyl chloride. By applying the method based on periodic sampling of a heterogeneous reaction mixture from the reactor during the reaction and a gas chromatographic determination of unreacted monomers present in the sample, we studied the copolymerization system vinyl chloride-propene.[2] It was demonstrated[2] that by employing this method, the summary conversion copolymerization curves, conversion curves of the individual monomers, and their initial reaction rates can be obtained from a single experiment for a given composition of the monomeric mixture copolymerized according to a chosen procedure.

In this study the method was used to investigate the kinetic behavior of vinyl chloride in reaction mixtures containing various amounts of 1-butene and 1-pentene (5, 10, 15, 20, 25, 30 mass%). The results obtained are compared with the kinetic behavior of the copolymerization system vinyl chloride-propene; the reliability of the method is discussed.

MATERIALS

The copolymerizations were carried out using chemicals in amounts given below:

Vinyl chloride (Spolana, Neratovice, 205.2–151.2 g), impurities content 90 ppm at most (H_2O 73 ppm, methyl chloride 9 ppm, vinylacetylene 6.5 ppm, 1,3-butadiene 5 ppm, ethyl chloride 4 ppm, iron < 0.5 ppm). 1-Butene

CCC 0021-8995/87/082681-07$04.00

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(Merck-Schuchardt, München, 10.8–64.8 g), purity 99% (isobutene 0.7%, 1,3-butadiene 0.1%). 1-Pentene (Merck-Schuchardt, München, 10.8-64.8 g), purity 97%. Dicetylperoxydicarbonate (Kema-Nord, Stockholm, 0.80140 g), peroxide content 73.5%, active oxygen content 2.2%. Hydroxypropylmethylcellulose (Dow Chemical Co., 13.12 g; 3.8% solution), viscosity of 2% solution 4.598×10^{-2} Pa.s. Distilled water (515 g).

METHODS

The experimental arrangement used has been described earlier.[1,2] The copolymerizations were carried out for 18 h at 55 ± 0.1°C, at the stirrer revolutions 500 per minute. The volume of the sample varied in the range of tens of microliter, depending on the size of the sampling slot used. Chromatographic records of vinyl chloride obtained during individual copolymerizations were evaluated as described earlier.[1,2] The known time dependencies of the chromatographically determined amounts of vinyl chloride in the sample were used in calculating the initial reaction rates of vinyl chloride.

The copolymers obtained were decanted with 2 dm^3 distilled water and washed on a fritted disc S 1 with ca. 1 dm^3 distilled water. Samples dried to constant weight at 60°C were weighed and sifted on a 0.250 mm sieve.

The 1-olefin content in the copolymer was calculated from the carbon determination by elemental analysis and using an automatic C-H-N analyzer (Perkin-Elmer, Model 240).

The intrinsic viscosity was measured by the standard dilution method in tetrahydrofuran.

RESULTS AND DISCUSSION

In series of copolymerizations of vinyl chloride with propene, it has been confirmed that the gas chromatographic determination of unreacted monomers during the polymerization is suited not only for an investigation of the

TABLE I
Results of Copolymerizations of Vinyl Chloride with 1-butene

$[M_2]^a$	$[M_2]^b$	C_{VCM}^c	C_{Bu}^d	C_w^e	$[\eta]^f \times 10^{-2}$	A^g
(% mol)		(%)			(cm^3/g)	(% from yield)
6.0	2.1	58.4	19.8	56.3	0.592	2.2
11.4	4.7	34.4	13.0	32.2	0.415	7.2
16.7	6.5	25.1	8.6	22.6	0.369	14.0
21.8	8.5	19.4	6.5	16.8	0.332	20.1
27.4	10.8	14.5	4.6	12.0	0.216	24.1
32.8	12.9	6.1	2.4	5.0	0.158	25.9

[a] Content of 1-olefin in the initial mixture of monomers.
[b] Olefin content in the copolymer.
[c] Final conversion of vinyl chloride calculated from (b), (e).
[d] Final conversion of 1-butene calculated from (b), (e).
[e] Final total conversion of monomers determined gravimetrically.
[f] Intrinsic viscosity.
[g] Residue on the sieve 0.250 mm.

TABLE II
Results of Copolymerizations of Vinyl Chloride with 1-Pentene

$[M_2]$	$+M_2+$	C_{VCM}	C_{Pe}	C_w	$[\eta] \times 10^{-2}$	A
(% mol)			(%)		(cm^3/g)	(% from yield)
4.6	2.0	63.2	21.5	62.2	0.508	4.5
9.1	3.8	46.3	18.5	43.5	0.388	8.8
13.8	6.3	29.9	12.6	27.3	0.268	11.6
18.2	8.1	23.2	9.2	20.4	0.227	21.7
22.9	10.0	17.2	6.4	14.5	0.225	24.0
27.8	12.3	12.4	4.5	10.0	0.197	27.3

Symbols as in Table I.

course of vinyl chloride homopolymerization,[1] but also for study of its copolymerization with propene.[2] Therefore, we tried this method to study the kinetic behavior of the copolymerization systems vinyl chloride-1-butene and vinyl chloride-1-pentene. However, our preliminary results showed a limitation of this method. Repeated experiments revealed that a sufficiently fast and quantitative desorption of 1-butene and 1-pentene is not achieved from the withdrawn sample in our experimental arrangement,[1] even when the temperature for monomer desorption was increased above 100°C. Hence, we focused our attention on the vinyl chloride kinetic data evaluation. The data on its kinetic behavior can be obtained with accuracy and reproducibility reported earlier[1] and together with analytical and gravimetric data (copolymer compositions, final conversions; Tables I and II) enable us to describe the copolymerizations.

Kinetic Behavior of Vinyl Chloride During the Copolymerization with 1-Butene and 1-Pentene.

Similarly to the system vinyl chloride propene,[2] a pronounced slowing down of the polymerization process was observed with both pairs of monomers also at low concentration of 1-olefin, compared with the homopolymerization of vinyl chloride, along with the elimination of the autoacceleration effect typical of the homopolymerization. The conversion curves shown in Figures 1 and 2 were constructed with direct use of chromatographic data, uncorrected[1,2] with respect to the amount of vinyl chloride present at the given degree of conversion in the vapor space of the reactor. The conversion curves thus obtained are analogous to corrected curves[1,2] and, therefore, they were used for a relative comparison of the kinetic course of the copolymerizations carried out under the same reaction conditions.

A closer quantitative insight into the copolymerizations is provided by the initial reaction rates (Table III, Fig. 3). With increasing concentration of 1-olefin in the initial monomeric mixture, the initial reaction rate of vinyl chloride decreases markedly in both pairs of monomers. In the copolymerizations of vinyl chloride with both 1-butene and 1-pentene the initial reaction rates of vinyl chloride are comparable (and considerably lower than in the system vinyl chloride propene[2]), and the differences between them do not
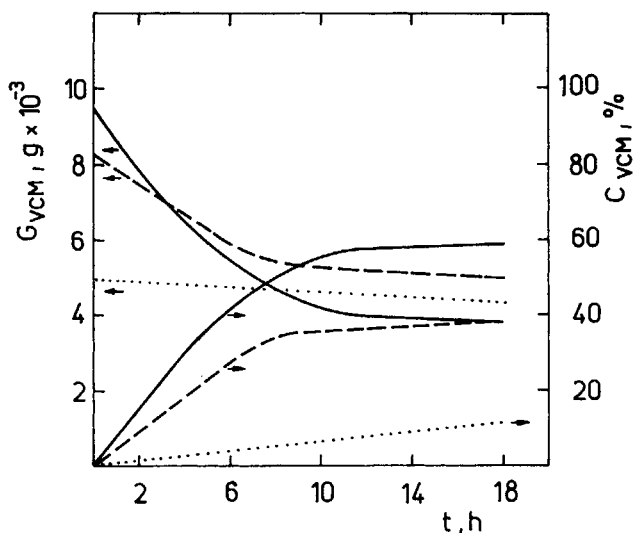
Fig. 1.   Time dependence of chromatographically determined amount of vinyl chloride (G_{VCM}) and of the degree of conversion (C_{VCM}) reached for 5.4 (——), 10.5 (– – –), 30.4 (...) mass % of 1-butene in the initial monomeric mixture.

virtually exceed the error of their determination.[1] These conclusions are in good agreement with the values of the final conversions.

When estimating the effect of the individual 1-olefins on the course of copolymerization, it may be concluded, by using total conversions of this reaction related to the same molar comonomer concentrations in the initial mixture, that the total reaction rate of copolymerization of the pairs of
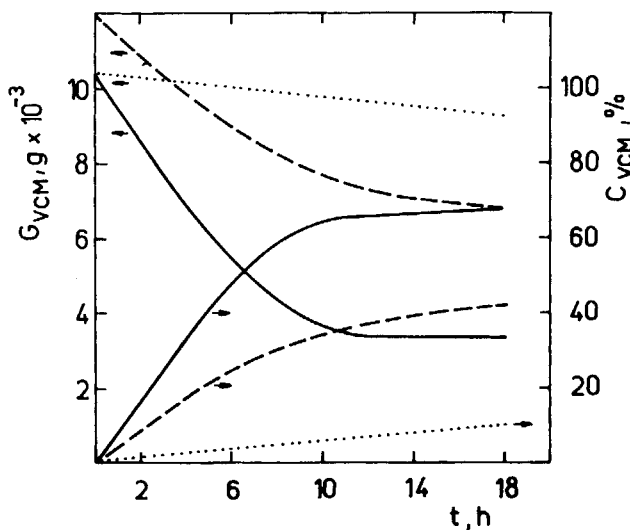

Fig. 2.   Time dependence of chromatographically determined amount of vinyl chloride (G_{VCM}) and of the degree of conversion (V_{VCM}) reached for 5.1 (——), 10.0 (– – –), 30.1 (...) mass % of 1-pentene in the initial monomeric mixture.

TABLE III
Initial Reaction Rates of Vinyl Chloride in the Copolymerization with 1-Butene and 1-Pentene

1-Butene[a] (% mol)	6.0	11.4	16.7	21.8	27.4	32.8
$\dfrac{-\Delta[VCM]}{\Delta t}$ $(10^{-6}\,mol/dm^3\,s^{-1})$	68.3	34.2	13.3	8.4	6.9	3.0
1-Pentene[a] (% mol)	4.6	9.1	13.8	18.2	22.9	27.8
$\dfrac{-\Delta[VCM]}{\Delta t}$ $(10^{-6}\,mol/dm^3\,s^{-1})$	76.7	47.1	11.9	8.4	7.4	5.7

[a]1-Olefin content in the initial monomeric mixture.

monomers under investigation decreases in the following order (which remains unchanged throughout the reaction):

VCM-propene > VCM-1-butene $\doteq$ VCM-1-pentene

This finding may be explained by using views analogous to those reported in Refs. 3, 4. Similar to propene, 1-butene and 1-pentene are less reactive monomers in the copolymerization system than vinyl chloride; their addition to the propagating polymer radicals proceeds at a lower rate than the addition of vinyl chloride. In the copolymerization of vinyl chloride with propene the chain transfer to propene, in which the allyl radical acting as a degradation transfer agent is formed,[3,4] also contributes to the reduction of the overall reaction rate. The formation of thermodynamically stable radicals of the same
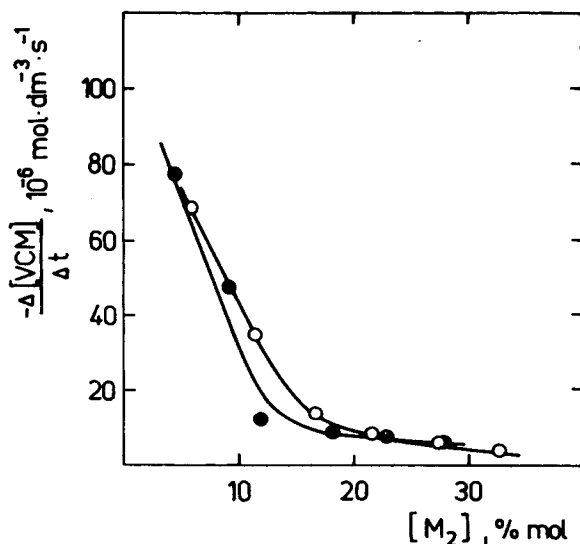

Fig. 3.   Initial reaction rates of vinyl chloride determined in the copolymerization of vinyl chloride with various contents of 1-butene (○) and 1-pentene (●) in the initial monomeric mixture.

type may be expected also for higher 1-olefins. In such cases the resonance stability of the radicals is probably enhanced by the positive inductive effect of the alkyl present, which obviously plays an unfavorable role in the copolymerization as a steric hindrance. Allyl radicals have a stronger tendency toward termination of the propagating chain than toward the onset of propagation of a new chain, because addition of the monomer would lead to an energetically richer radical. Degradative chain transfer, which prevents the radical homopolymerization of olefins, is obviously operative also in the copolymerization, and seems to be—along with the different rates of propagation—yet another cause of the observed decrease in the reaction rate and molar mass.

Characterization of the Copolymers of Vinyl Chloride with 1-Butene and 1-Pentene

The 1-olefins under investigation reduce the intrinsic viscosity of copolymer solutions compared with the homopolymer of vinyl chloride; the decrease observed is (similarly to propene)[2] pronounced already at low comonomer concentrations in the initial monomeric mixture (Tables I and II). If the intrinsic viscosity is related to the same molar contents of the comonomer in the copolymer, the following dependence may be obtained in the whole concentration range under investigation for the copolymers taken for comparison:

$$[\eta]_{\text{VCM-propene}} > [\eta]_{\text{VCN-1-Butene}} > [\eta]_{\text{VCM-1-pentene}}$$

At the same time, with increasing content of 1-olefins in the initial monomeric mixture, the stability of suspension gradually decreases. In all cases, however, a homogeneous product without agglomerates was obtained. The amounts of coarse polymer particles (> 0.250 mm) are higher in the vinyl chloride copolymerizations with 1-butene and 1-pentene (Tables I, II) than in the system vinyl chloride-propene.[2]

As follows from the comparison of comonomer content in the initial monomer mixture with its content in the copolymer, 1-butene and 1-pentene are incorporated in the polymer chain in comparable amounts. The difference between propene[2] and 1-butene lies within the limit of experimental error of the composition determination.

CONCLUSIONS

By summarizing the results obtained from the copolymerization systems vinyl chloride-1-butene and vinyl chloride-1-pentene, the following conclusions can be drawn:

1. The GC method used in these systems enables us to describe the kinetic behavior of vinyl chloride quickly and reliably.

2. The method is not suitable for kinetic investigations of 1-butene and 1-pentene because of slow and incomplete desorptions of these comonomers from the withdrawn samples.

3. 1-Butene and 1-pentene, even when present in the reaction system at low concentrations, slow down the polymerization process in a comparable manner with respect to the vinyl chloride homopolymerization.

4. Slowing of the polymerization process is more pronounced than in the system vinyl chloride-propene.[2]

5. The intrinsic viscosities of copolymer solutions indicate that at the same molar contents of comonomer in the copolymer the values measured for 1-butene are higher than those for 1-pentene, but lower than those determined earlier for propene.[2]

6. 1-Butene and 1-pentene are incorporated in the polymer chain in comparable amounts. No significant difference was found by comparison with the values found earlier for propene.[2]

7. The stability of suspension decreases in the order VCM - propene > VCM-1-butene ≐ VCM -1-pentene, and with increasing amount of 1-olefin.

References

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