The Copolymerization of Vinyl Chloride with 1-Olefins. V. Heat Stability of Copolymers of Vinyl Chloride with Propene, 1-Butene, and 1-Pentene

ZDENĚK MRÁZEK,* RUDOLF LUKÁŠ, and OLGA PŘÁDOVÁ

Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, 162 06 Prague 6, Czechoslovakia

SYNOPSIS

Copolymers of vinyl chloride with propene, 1-butene, and 1-pentene containing 2–15 mol % of 1-olefinic structural units were prepared. The copolymers were dehydrochlorinated at 180°C in an inert atmosphere; the amount of hydrogen chloride split off was determined by continuous potentiometry. The results show that the heat stability of propene, 1-butene, and 1-pentene copolymers containing the same amount of 1-olefinic structural units does not differ significantly. Compared with the homopolymer of vinyl chloride, it is favorably affected by the presence of 1-olefinic structural units in poly(vinyl chloride) (PVC) chains. On the other hand, however, the heat stability of copolymers is impaired by the higher content of structural defects able to initiate the dehydrochlorination reaction. These structural defects, probably represented by chloroallyl groups, are formed in the copolymers during their synthesis. At the beginning of heating, structural defects produce intensive dehydrochlorination and, therefore, copolymers of vinyl chloride with 1-olefins if processed appear to be less thermally stable than does PVC.

INTRODUCTION

In our earlier papers, we investigated the kinetic course of the copolymerization of vinyl chloride with propene,[1] 1-butene, and 1-pentene.[2] Later, other samples of these copolymers were tailored so that their parameters allowed us to characterize the effect of the individual 1-olefins and of molecular weight of the copolymers on rheological and mechanical properties of these materials.[3]

A chosen assembly of such samples was investigated with respect to heat stability by using a continuous potentiometric determination of hydrogen chloride. The amount of hydrogen chloride released and the time dependencies thus derived were used to describe the dehydrochlorination process of the copolymers of vinyl chloride with 1-olefins differing in the content and length of the comonomer and to compare this process with the behavior of the homopolymer of vinyl chloride. Experimental data thus obtained are discussed particularly in relation to structural defects introduced into the copolymer during the synthesis.

EXPERIMENTAL

Sample Preparation

Heat stability was investigated using two groups of samples. Each of these groups was prepared under different experimental conditions. Samples in the first group differing in the comonomer and its content in the copolymer were obtained in a reactor (vol 1 dm^3, 55 ± 0.1°C, 500 rpm) using the following recipe (values in parentheses are related to the preparation of the reference sample of the homopolymer of vinyl chloride): 205.2–151.2 g (216.0 g); 1-olefin, 10.8–64.8 g (0.0 g); dicetylperoxydicarbonate, 0.80140 g (0.20035 g); hydroxypropyl methyl cellulose, 13.12 g, 3.8 wt % aqueous solution; and distilled water, 515 g. Basic information on samples thus prepared is presented in Table I.

Table I   Copolymers of Vinyl Chloride with 1-Olefins Prepared under Identical Reaction Conditons

Sample	$[M_2]^a$ (mol %)	$\{M_2\}^b$ [mol %]	Conversion (%)	$[\eta]^c \times 10^{-2}$ (cm^3 g^{-1})
1	7.9 P	3.1	84.0	0.658
2	19.9 P	7.6	65.3	0.497
3	39.5 P	14.4	27.1	0.315
4	6.0 Bu	2.1	56.3	0.592
5	16.7 Bu	6.5	22.6	0.369
6	32.8 Bu	12.9	5.0	0.158
7	4.6 Pe	2.0	62.2	0.508
8	18.2 Pe	8.1	20.4	0.227
9	27.8 Pe	12.3	10.0	0.197
10^d	—	—	88.4	0.852

[a] Content of 1-olefin in the starting mixture of monomers (P, propene; Bu, 1-butene; Pe, 1-pentene).
[b] Content of 1-olefinic structural units in the copolymer.
[c] Intrinsic viscosity.
[d] Reference homopolymer of vinyl chloride.

The other group of samples was prepared in a reactor, 5 dm^3 in volume, under such conditions that the content of the comonomer and molecular weight of the samples were comparable. Dosed into the reactor each time were 1237 g of monomers, 2933 g of distilled water, and 142.5 g of hydroxypropyl methyl cellulose in the form of a 3.8 wt % aqueous solution. The temperature was regulated with an accuracy ±0.3°C; revolutions of the stirrer were 500 min^{-1}. Further data regarding conditions of synthesis and basic parameters of the copolymers are summarized in Table II.

A detailed description of the polymerization apparatus, the working procedure, and specification of

the raw materials used have already been published.[1-3]

MATERIALS AND METHODS

The composition of the copolymers was determined from carbon determinations by elemental analysis using a C-H-N automatic analyzer (Perkin-Elmer, Model 240). The intrinsic viscosities were determined by the standard dilution method in tetrahydrofuran at 25°C; Fikentscher's K-values[4] were also determined by the usual procedure (Czechoslovak standard 643200). The weight average molecular

Table II   Copolymers and Homopolymers of Vinyl Chloride Prepared under Various Reaction Conditions

Sample	DCPD^a (g)	Temperature (°C)	Time (g)	$[M_2]^b$ (mol %)	$[M_2]^c$ (mol %)	Conversion (%)	K value^d	$\bar{M}_w^e$
11	4.448	51.0	11.5	7.5 P	4.5	78.9	57.6	—
12	4.448	70.0	8.5	8.5 P	4.3	64.9	46.8	33.500
13	8.896	51.0	14.0	8.5 Bu	4.2	47.6	46.2	35.700
14	8.896	51.0	16.0	8.6 Pe	4.2	59.3	46.4	36.000
15	0.692^f	68.5	6.0	—	—	78.5	46.2	37.000
16	1.972	51.0	5.5	—	—	79.1	71.0	—

[a] Amount of dicetylperoxydicarbonate.
[b] Content of 1-olefin in the starting mixture of monomer (P, propene; Bu, 1-butene; Pe, 1-pentene).
[c] Content of 1-olefinic structural units in the copolymer.
[d] Fikentscher's constant.[4]
[e] Weight average molecular weight.
[f] Dilauroyl peroxide (0.829 g) and trichloroethylene (30.5 g) was also added to the reaction mixture.

Table III   Amount of Released Hydrogen Chloride Determined in the Course of Dehydrochlorination

Sample[a]	Content of 1-olefin[b] (mol %)	Dehydrochlorination in mol HCl $\times$ 10^6 at a time t (min)					
		10	20	30	40	50	60
1	3.1 P	2.88	5.41	7.62	9.75	11.60	13.39
2	7.6 P	4.05	7.03	9.56	11.87	14.25	16.59
3	14.4 P	6.86	10.92	14.06	16.82	19.34	22.00
4	2.1 Bu	2.55	4.79	6.63	8.50	10.22	11.87
5	6.5 Bu	6.22	9.65	12.23	14.51	16.51	18.34
6	12.9 Bu	9.03	14.91	18.96	21.93	24.41	26.59
7	2.0 Pe	2.50	4.59	6.41	8.17	9.77	11.40
8	8.1 Pe	5.20	8.60	11.05	13.30	15.27	17.15
9	12.3 Pe	7.23	13.39	17.39	20.53	23.36	25.72
10	—	1.68	3.80	6.22	8.71	11.15	13.62

[a] Amount of sample 200 mg.
[b] P, propene; Bu, 1-butene; Pe, 1-pentene.

weights were obtained by the light-scattering method. Dilute solutions of chosen samples dissolved in tetrahydrofuran were measured in polarized light, with a wavelength of 5461 nm, in the angular range 30–150° (Photo-Gonio-Diffusiometer, Fica, Model 42000).

The heat stability of all samples was measured in an inert atmosphere (nitrogen) by a continuous potentiometric determination of split-off hydrogen chloride.[5] An automated apparatus was used[6]; the flow rate of nitrogen as the carrier gas was 5.5 cm^3 s^{-1}. A glass degradation cell with the sample in powder form (200 mg) placed on a platinum dish was heated by an eutectic nitrate–nitrite salt bath to 180 $\pm$ 0.1°C. The results obtained are expressed through the number of moles of split-off hydrogen chloride (Tables III and IV). For some selected samples, Figure 1 presents dehydrochlorination

curves that show the dependence of the rate of dehydrochlorination on time, $\Delta\xi/\Delta t = f(t)$, where ξ is the conversion of dehydrochlorination expressed as a mol fraction. Because of considerable differences in copolymer composition, the rates of dehydrochlorination are related to the weight of poly(vinyl chloride) (PVC) structures in the copolymer.

RESULTS AND DISCUSSION

Heat Stability of Copolymers of Vinyl Chloride with Various Content of the 1-Olefinic Component

Samples of copolymers containing various amounts of propene, 1-butene, and 1-pentene, including the reference homopolymer of vinyl chloride, were pre-

Table IV   Amount of Released Hydrogen Chloride Determined in the Course of Dehydrochlorination

Sample[a]	Content of 1-olefin[b] (mol %)	Dehydrochlorination in mol HCl $\times$ 10^6 at a time t (min)										
		10	20	30	40	50	60	70	80	90	100	110	120
11	4.5 P	2.59	4.81	6.85	8.73	10.56	12.31	14.00	15.58	17.09	18.54	20.01	21.45
12	4.3 P	2.78	5.91	8.86	11.63	14.54	16.96	19.42	21.78	24.06	26.14	28.36	30.48
13	4.2 Bu	3.33	5.75	8.06	10.22	12.22	14.15	15.99	17.75	19.42	21.08	22.70	24.33
14	4.2 Pe	3.61	5.91	7.97	9.88	11.76	13.57	15.18	16.85	18.43	20.03	21.56	23.02
15	—	2.46	5.69	9.30	13.33	16.93	20.92	24.61	28.40	32.24	36.00	39.99	43.47
16	—	1.62	3.99	6.93	9.74	12.80	15.82	18.79	21.90	24.82	27.68	30.67	33.64

[a] Amount of sample 200 mg.
[b] P, propene; Bu, 1-butene; Pe, 1-pentene.
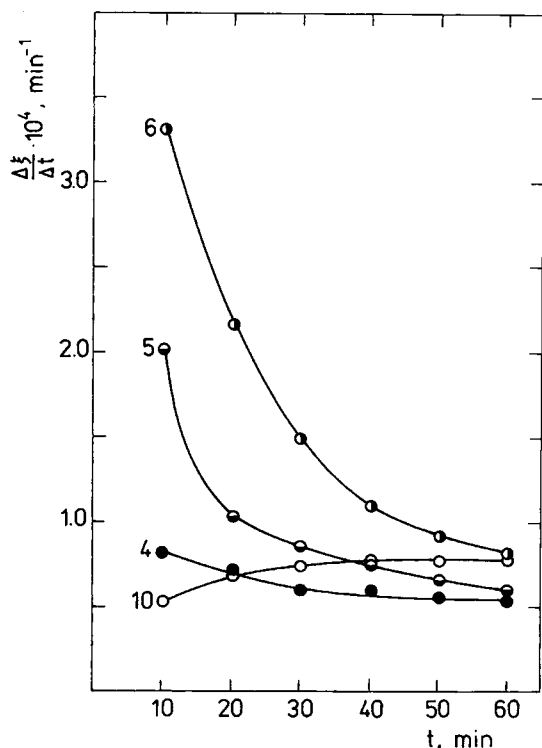
Figure 1 Time dependencies of the rate of dehydrochlorination of copolymers of vinyl chloride with 1-butene. Content of 1-butene: 4, 2.1 mol %; 5, 6.5 mol %; 6, 12.9 mol %; 10, PVC.

pared using the same recipe and reaction conditions (see sample preparation and Table I). However, the presence of the individual 1-olefins at various concentrations in the reaction mixture affects considerably the kinetics of these copolymerizations and molecular weight of the copolymers formed.[1,2] Hence, different final conversions are reached with the same copolymerization time. Consequently, the samples may differ from each other in their morphology (cf., e.g., the dependence of porosity on conversion) and, of course, also in some physicochemical parameters due to their different composition and different molecular weight. Compared with poly(vinyl chloride), copolymers of vinyl chloride with these 1-olefins generally have a lower glass transition temperature, which decreases also with increasing content of olefinic structural units.[3] With respect to the conditions used in the experiments, and also because at the temperature of measurement grains of the copolymers pass, at least partly, into the annealed state, or even form melt, the effect of a different morphology of copolymer particles on the results of measurements can virtually be ruled out. On the contrary, just the lower glass transition temperature and lower molecular weight of copolymers

with a higher content of 1-olefin may participate in a more intensive splitting off of hydrogen chloride. However, compared to the sample in the powder form, the melt contains more hydrogen chloride, which also leads to a more efficient catalysis of dehydrochlorination.[7]

The heat stability of copolymers with various amounts of 1-olefin may be characterized based on dehydrochlorination data given in Table III. The amount of split-off hydrogen chloride at the beginning of heat exposure (after 10, 20, 30 min) is higher in the case of all copolymers under study than in the reference PVC sample. The relatively highest difference in the dehydrochlorination behavior expressed through the ratio mol $HCl_{copolymer}$/mol HCl_{PVC} is observed after 10 min of heating. With increasing time of dehydrochlorination, this ratio decreases, and, e.g., after 60 min, the samples of copolymers with a low amount of 1-olefins (ca. 2–3% mol) appear to be thermally more stable than PVC. This situation can be easily observed in Figure 1, which shows the time dependencies of the rate of dehydrochlorination of copolymers of vinyl chloride with 1-butene. One can see in Figure 1 that compared with PVC these copolymers are dehydrochlorinated at the beginning of heating at high rates, which, however, decrease quite quickly. With samples having a lower content of 1-butene (2.1 and 6.5 mol %), after 25 or 40 min, respectively, they reach lower values than those that correspond to a constant rate of dehydrochlorination of the reference PVC sample. The dehydrochlorination curves of copolymers resemble by their shape the dehydrochlorination process of PVC samples enriched in chloroallyl structures[8] and demonstrate that copolymer samples contain some structural defects that only transiently act in the sense of the initiation of dehydrochlorination.[9] The formation of such defects should be sought in the synthesis of copolymers, i.e., in the copolymerization process, in which, due to the increased initiator concentration, side reactions of radicals arising by the decomposition of the initiator may also play a more important role.[10] This reaction consists of an attack of the initiator radical on PVC chains and leads to the dehydrochlorination of regular structural PVC units accompanied by the formation of chloroallyl structures. In the copolymerization process, 1-olefins also behave as degradative transfer agents[11]; hence, the possible dehydrochlorination activity of radicals thus formed cannot be ruled out either. Based on the results reported earlier, however,[10] one may assume that structural defects introduced into the copolymers are probably represented by chloroallyl structures.
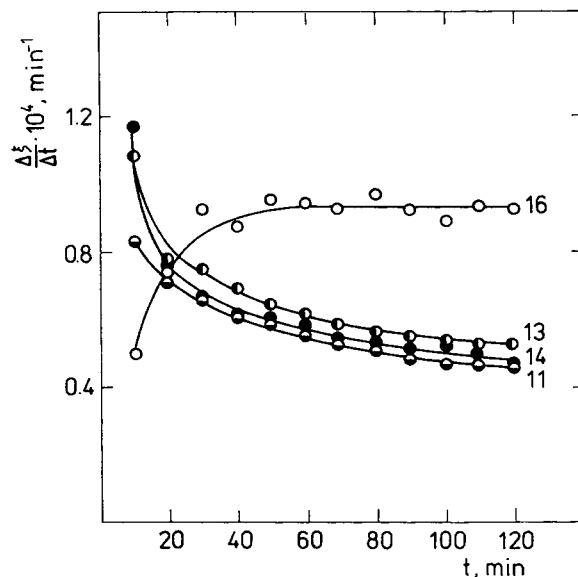
COPOLYMERS OF VINYL CHLORIDE WITH 1-OLEFINS. V

The same conclusions follow from the time dependencies of the rates of dehydrochlorination of propene and 1-pentene copolymers that have the same character. Hence, it may be stated that the stabilizing effect of isolated 1-olefinic structural units[12] (increased termination of propagating polyenes) is counteracted by an intensive dehydrochlorination at the beginning of heating of the samples that is caused by defects introduced into the copolymer during its synthesis. Copolymers with a higher content of 1-olefins have more labile structures and also pass more readily into the melt, where the catalysis with hydrogen chloride is more operative than in the solid phase.

In the characterization of the heat stability of polymers with respect to the usual practice, the conclusive role is played by their behavior at the beginning of thermal treatment, at times corresponding to the processing technologies. Bearing in mind this fact, directly related to heat stabilization, one may say (a) that the copolymers discussed above have poorer heat stability than does PVC and (b) that their heat stability becomes poorer with increasing content of 1-olefin in the copolymer.

Effect of the Length of 1-Olefin on the Heat Stability of Copolymers of Vinyl Chloride

We tried to examine the effect of the individual 1-olefins on the heat stability of their copolymers with vinyl chloride using an assembly of samples of the same composition and of a comparable molecular weight. It can be seen in Table II that samples having such parameters were obtained by the suspension copolymerization under various reaction conditions. In view of the features of copolymerization of vinyl chloride with propene,[1] 1-butene, and 1-pentene,[2] different reaction temperatures and times had to be used, and the content of 1-olefin in the starting mixture of monomers also had to be different. The results of dehydrochlorination measurements of these samples, supplemented by the reference homopolymer of vinyl chloride, and also by PVC and by the copolymer of vinyl chloride with propene, which were also synthesized at 51.0°C, are given in Table IV and Figure 2.

Dehydrochlorination data (Table IV and Fig. 2) demonstrate the same dependencies as those discussed above for the case of copolymers of vinyl chloride with a different content of 1-butene. To confirm the stabilizing effect of 1-olefinic structural units, the samples were dehydrochlorinated for 120 min. After this time, the rates of dehydrochlorination of copolymers become roughly half the constant

Figure 2 Time dependencies of the rate of dehydrochlorination of copolymers of vinyl chloride with 1-olefins having the same content of the 1-olefinic component (4.3 ± 0.2 mol %).

rate of dehydrochlorination of the reference PVC sample (Fig. 2). If, e.g., the heat stability of these copolymers were evaluated after 120 min of heating on the basis of split-off hydrogen chloride (Table IV), all the copolymers just mentioned would possess a higher heat stability than does the PVC sample. Hence, after a long-term heat exposure, total changes in the structure of these samples due to the higher temperature are smaller than with PVC.

The real course of dehydrochlorinations (Fig. 2) in the copolymers, however, is again nonuniform in time, with an intensive hydrogen chloride elimination at the beginning of thermal treatment. It may again be stated that due to the higher content of defective structures these copolymers of vinyl chloride with 1-olefins are less heat resistant in the usual applications than is PVC.

At the same time, the amounts of hydrogen chloride split off by the pair of copolymers vinyl chloride-propene (Table IV, samples 11 and 12) and homopolymers of vinyl chloride (samples 15 and 16) indicate a considerable dependence of heat stability on the reaction temperature. Compared with this factor, the effect of different molecular weight (if any) can be neglected. Our next study is therefore concentrated on detailed connections between conditions of the synthesis of copolymers and their heat stability.

For the sake of comparison, Figure 2 shows the copolymer of vinyl chloride with propene prepared

at the same reaction temperature as were the other samples. The kinetic curves suggest that the dehydrochlorination of the individual copolymers proceeds virtually in the same way. A certain trend can be found if one compares the rates of dehydrochlorination at 10 min reaction time. In this case, however, the propene copolymer is the most stable, followed by the 1-butene copolymer, with the 1-pentene copolymer being the least stable. This fact, which is probably related to the different concentrations of defects, may be quite random, however, if the effect of the reaction conditions is not known in any detail.

The results obtained so far suggest that the copolymers under study possess not only comparable rheological and mechanical properties,[3] but also that the heat stability is similar. The kinetics of synthesis of the copolymers of vinyl chloride with propene, 1-butene, and 1-pentene, however, is most favorable for the copolymerization of vinyl chloride with propene.[1,2] Hence, the copolymers of vinyl chloride and propene seem advantageous predominantly for economic reasons.

CONCLUSIONS

The behavior of copolymers of vinyl chloride with propene, 1-butene, and 1-pentene at elevated temperatures was investigated by using the method of a continuous potentiometric determination of hydrogen chloride in an inert atmosphere. The results obtained are compared with the dehydrochlorination behavior of PVC and lead to the following conclusions:

1. At the beginning of heating, the copolymers dehydrochlorinate at higher rates than do the PVC samples used for comparison. The rates of dehydrochlorination decrease quickly, reaching lower values sometime after those of the constant rate of dehydrochlorination of reference PVC samples.
2. The high rates of dehydrochlorination of copolymers at the beginning of heating are due to an increased content of defective structures able to initiate the dehydrochlorination.
3. Defective structures are introduced into polymer chains during the copolymerization

process, probably as a result of a side reaction of radicals formed by the decomposition of the initiator or by a degradative transfer of 1-olefins.
4. Similarity between the dehydrochlorination curves of copolymers and the dehydrochlorination behavior of PVC resins enriched in chloroallyl structures suggests that the defective structures introduced into the copolymers are most probably chloroallyl structures.
5. The expected stabilizing effect of 1-olefinic structural units can easily be observed only after long-term heat degradation.
6. Because of the occurrence of defective structures, the copolymers of vinyl chloride with 1-olefins appear as thermally less stable in processing.
7. The heat stability of copolymers of vinyl chloride with propene, 1-butene, and 1-pentene do not differ much from each other.

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