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P. Hildenbrand[a]; W. Ahrens[a]; F. Brandstetter[a]; P. Simak[a]
[a] BASF Aktiengesellschaft, Ludwigshafen, West Germany

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The Formation of Terminal Double Bonds in Vinyl Chloride Polymerization

P. HILDENBRAND, W. AHRENS, F. BRANDSTETTER, and P. SIMAK

BASF Aktiengesellschaft
D-6700 Ludwigshafen, West Germany

ABSTRACT

The determination of double bonds in PVC is achieved with an increased accuracy in comparison with earlier methods by the addition of iodine monochloride (Wijs reaction) to PVC coupled with x-ray fluorescence analysis to determine the iodine content of the polymer. The number of double bonds per unit weight of polymer increases on increasing the polymerization temperature and is proportional to the number of polymer molecules. It is not affected, however, by the presence of the chain transfer agent tetrahydrofuran (THF). At the technically important polymerization temperatures of 30 to 80°C and in the absence of the chain transfer agent, 0.9 double bonds per polymer molecule are found. The number of double bonds per polymer molecule is lowered using the chain transfer agent THF. These results support the theory that the chain transfer to monomer and possibly the termination reaction are coupled with the formation of terminal double bonds. Contributions by internal double bonds formed by dehydrochlorination of the polymer during polymerization are excluded by investigating the $Cl^{\ominus}$ content of the water phase in the oxygen-free VC suspension polymerization. No hydrogen chloride is formed. In IR spectra of PVC, the stretching vibration of the double bonds is detected at 1667 cm^{-1} by the correlation of the double bond contents and the intensities

of the absorption bands. The stretching vibration at 1667 cm^{-1} is in accordance with those of model compounds with a 1-chloro-2-alkene structure.

INTRODUCTION

The relatively low thermal stability of PVC in comparison with model compounds such as 2,4-dichloropentane [1] is generally attributed to labile chlorine atoms at defects in the PVC chain [2]. The most important of these defects is thought to be the double bond with an allylic chlorine structure [3]. In principle, double bond defects could arise from both the polymerization mechanism of VC and statistical dehydrochlorination in the polymer chain.

Both radical transfer from polymer radical to monomer and disproportionation of polymer radicals give rise to terminal double bonds. Some of the chain transfer mechanisms discussed in the literature [4-11] are shown in Fig. 1. The term "terminal double bonds" is used to represent double bonds standing at or close to the ends of the chain. This is demonstrated in Structures [a] to [d] in Fig. 1.

In contrast to the chain transfer reaction and the disproportionation of polymer radicals, statistical dehydrochlorination of PVC would result mainly in internal double bonds (Fig. 2).

The structure of double bonds in low molecular weight PVC has been investigated by Petiaud et al. [8] and Schwenk et al. [11] using NMR spectroscopy. Their results supported the assumption of terminal double bonds with a 1-chloro-2-alkene structure (Structure d in Fig. 1). It is the intention of this paper to give experimental proof for the formation and structure of double bonds in high molecular weight PVC.

Since a direct proof of the double bond structure in high molecular weight PVC using spectral methods has failed due to the low concentration of the double bonds, our examination was begun using chemical methods. To determine the total double bond content of PVC a modified Wijs reaction was used. Terminal double bonds are expected to be related to the number of polymer molecules. Internal double bonds formed by dehydrochlorination are expected to be related to the evolution of hydrogen chloride during VC polymerization. Therefore we have additionally determined the number of polymer molecules (molecular weight determination) and we have also investigated the evolution of hydrogen chloride during VC polymerization.

Knowing the double bond concentration enables us to identify the double bond absorption in the IR spectrum of PVC.

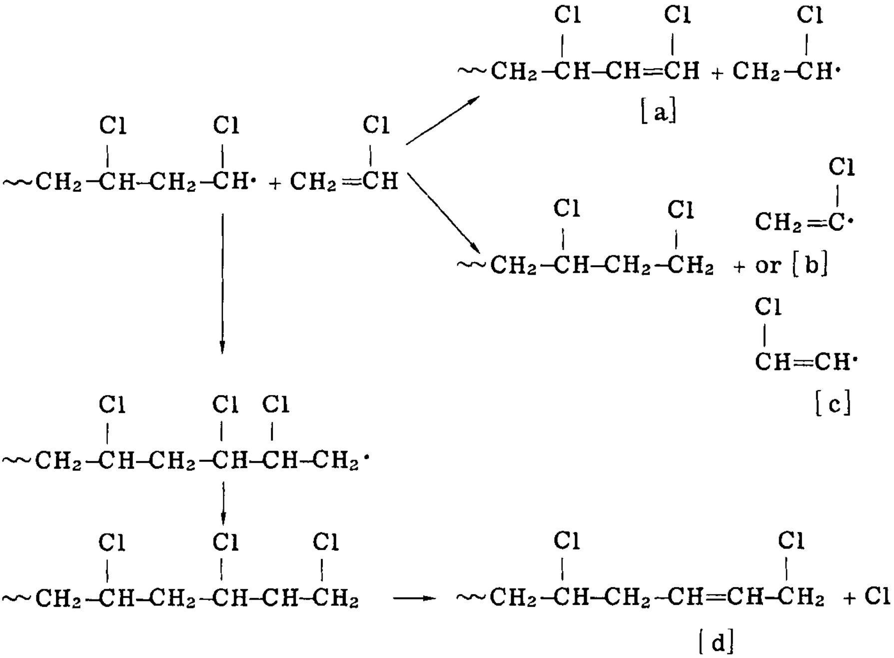

FIG. 1. Terminal double bonds formed by chain transfer reactions in VC polymerization.

$$\sim \mathrm{CH_2-\overset{Cl}{\overset{|}{C}}H-CH_2-\overset{Cl}{\overset{|}{C}}H-CH_2} \sim \xrightarrow{\mathrm{-HCl}} \sim \mathrm{CH_2-CH=CH-\overset{Cl}{\overset{|}{C}}H-CH_2} \sim$$

FIG. 2. Internal double bond formed by statistical dehydrochlorination of PVC.

FORMATION OF HYDROGEN CHLORIDE DURING VC POLYMERIZATION

In the commercial suspension polymerization of VC, hydrogen chloride is formed. This can easily be detected since the water phase becomes acidic and $Cl^{\ominus}$ ions are found. Formation of hydrogen chloride during VC polymerization has been shown to be due to the presence of oxygen [12, 13]. Oxygen reacts with VC to form peroxides, which decompose to carbon monoxide, formaldehyde, and hydrogen chloride. The presence of oxygen in VC polymerization gives rise to an approximately equimolar amount of $Cl^{\ominus}$ ions in the water phase of

TABLE 1

Polymerization no.	Oxygen (mol)	$Cl^{\ominus}$ in water phase (ppm) relative to VC		HCl formed (mol)
		Start	End	
1	0.36	46	1251	0.34
2	-	20	27	(2×10^{-3})

a suspension polymerization (see Table 1). To determine the amount of hydrogen chloride caused by dehydrochlorination of PVC during polymerization, we polymerized VC in suspension in the absence of oxygen. The $Cl^{\ominus}$-content of the water phase remains constant (compare Table 1) within experimental error limits (±10)ppm relative to VC). If dehydrochlorination of PVC occurs at all during polymerization, then it must be equal or less than the value of experimental error, i.e., at the most 0.06×10^{-5} mol of double bonds per g PVC.

DETERMINATION OF THE DOUBLE BOND CONCENTRATION IN PVC BY WIJS REACTION

To determine double bonds in PVC quantitatively, addition reactions, cleavage reactions, and nucleophilic substitution of allylic chlorine have been suggested in the literature [14-23]. Cleavage reactions [24] and nucleophilic substitution, however, appear to be influenced by side reactions, especially HCl elimination. Only the addition reaction of bromine, which determines the sum of terminal and internal double bonds, has generally been accepted [17, 18]. Disadvantages of bromine addition, however, are its long reaction time and the inaccuracy in back titrating the excess bromine. This led us to develop a simple, more accurate, and faster method of determining the double bonds in PVC involving an addition reaction using iodine monochloride (Wijs reaction) [25, 26]. A solution of iodine monochloride in trichloromethane is added at room temperature to a solution of PVC in 1,2-dichloroethane. The addition reaction is completed in 15 min. To remove excess iodine monochloride the polymer is precipitated and washed with methanol. The iodine content of the dried polymer, which is the measure of the double bond content, is determined using x-ray fluorescence analysis. Repeated measurements of the same PVC sample differ at most by 0.16×10^{-5} mol of double bonds per g PVC.

MOLECULAR WEIGHT DETERMINATION OF PVC USING GPC

Reciprocal molecular weight gives the number of polymer molecules per unit weight of polymer needed for correlation with the double bond content. The number-average molecular weight is determined by GPC in the usual way. The error limit of this method is found to be $\pm 0.1 \times 10^{-5}$ mol of polymer molecules per g PVC.

VC POLYMERIZATIONS AT DIFFERENT TEMPERATURES IN THE PRESENCE AND ABSENCE OF AN ADDITIONAL CHAIN TRANSFER AGENT

To obtain a correlation between the number of double bonds and the number of polymer molecules, VC was suspension polymerized at different temperatures with and without the addition of a chain transfer agent. The polymerization temperature was varied over the technically important range 30 to 80°C. As a chain transfer agent, 7% THF (relative to VC) was used.

Table 2 lists the experimental conditions of the VC polymerizations together with the corresponding yields and reaction times.

CORRELATION OF DOUBLE BONDS AND POLYMER MOLECULES

From the theory of VC polymerization, it is expected that terminal double bonds (D) are related to the number of polymer molecules (P). In Fig. 3, the results of model polymerizations are demonstrated in which chain growth has been terminated either by disproportionation or by recombination. For all polymerizations the same amount of monomer and only two initiator radicals were assumed. In the two first model polymerizations a chain transfer to monomer was excluded. In the following model polymerizations the frequency of chain transfer has been increased to one, two, three, etc. chain transfers per initiator radical. Terminal double bonds are formed by the radical transfer from polymer radical to monomer and by disproportionation of polymer radicals. The number of polymer molecules arises from initiation and chain transfer.

The number of double bonds can be represented by the same equation for both termination reactions:

$$D = P - 0.5I$$

$$\frac{D}{P} < 1$$

TABLE 2

Polymerization no.	T (°C)	THF (%) relative to VC	Initiator (%) relative to VC[a]	Yield (%)	Reaction time (h)
3	30	-	0.12 TMP-PA	47	7.4
4	40	-	0.10 TMP-PA	71	6.7
5	50	-	0.04 TMP-PA 0.04 TBPND	95	5.5
6	60	-	0.10 TBPND	80	4.0
7	70	-	0.02 TBPND 0.02 TBPPI 0.03 LPO	83	3.1
8	80	-	0.03 LPO 0.03 BP	84	4.5
9	40	7	Sample 4	38	7.0
10	50	7	Sample 5	57	7.5
11	60	7	0.06 TBPND	81	5.7
12	70	7	Sample 7	51	6.0
13	80	7	Sample 8	70	4.3

[a] TMP-PA: Trimethylpentylphenoxy-peracetate. TBPND: t-Butyl perneodecanoate. TBPPI: t-Butyl perpivalate. LPO: Lauroyl peroxide. BP: Benzoyl peroxide.

The dependence of the double bonds (D) on the number of polymer molecules (P) reduces to a linear function at constant initiation (I). Independent of the number of initiation steps, the number of double bonds per polymer molecule is predicted to be always smaller than one.

The experimental results of the double bond and molecular weight determinations of the PVC samples, which were polymerized according to the conditions of Table 2, are presented in Table 3 and Fig. 4. The number of double bonds and the number of polymer molecules are expressed in mol/g, since both are related to the unit weight of polymer.

The number of double bonds per unit weight of polymer increases on increasing the polymerization temperature, but is not affected by

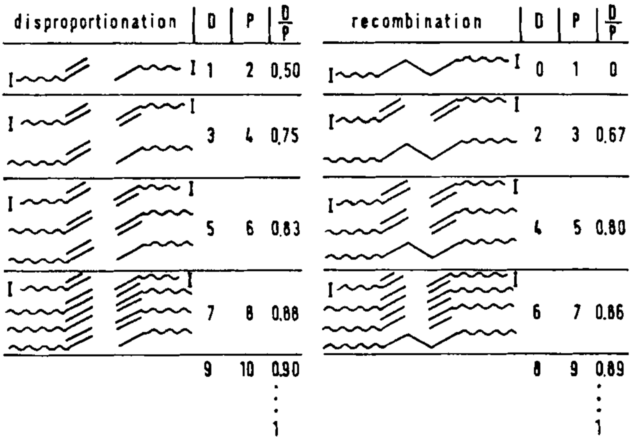

FIG. 3. Schematic correlation of double bonds (D) and polymer molecules (P).

TABLE 3

Polymerization no.	T (°C)	THF (%) relative to VC	M_n[a]	P × 10^5 (mol/g)	D × 10^5 (mol/g)	D/P
3	30	-	80,000	1.25	1.20	0.96
4	40	-	55,000	1.82	1.69	0.93
5	50	-	48,000	2.08	1.93	0.93
6	60	-	34,000	2.94	2.60	0.88
7	70	-	24,000	4.17	3.62	0.87
8	80	-	18,300	5.46	4.68	0.86
9	40	7	31,000	3.23	1.73	0.54
10	50	7	25,000	4.00	2.56	0.64
11	60	7	20,000	5.00	2.85	0.57
12	70	7	15,400	6.50	3.74	0.58
13	80	7	12,100	8.26	4.58	0.55

[a] M_n = number-average molecular weight.

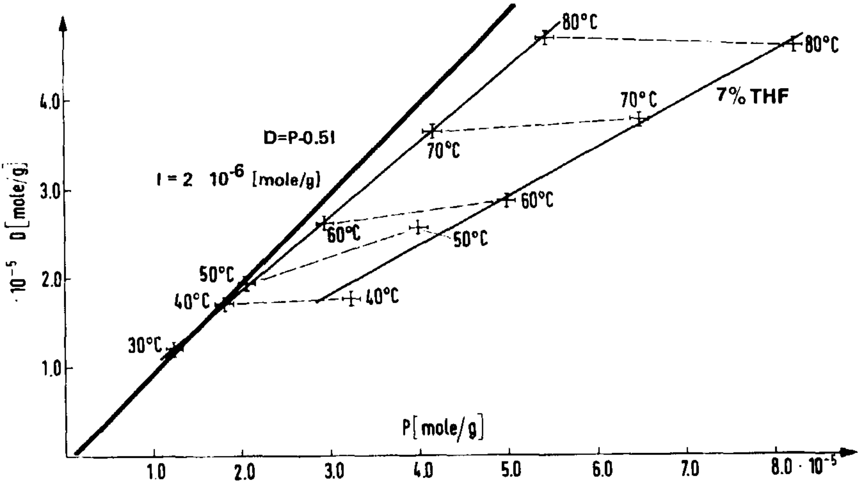

FIG. 4. Correlation of double bonds and polymer molecules.

the presence of the chain transfer agent THF within experimental error limits. The addition of THF does, however, result in more polymer molecules per unit weight of polymer (i.e., decreasing molecular weight). At polymerization temperatures in the technically important range, 30 to 80°C, and in the absence of an additional chain transfer agent about 0.9 double bonds per polymer molecule are found. The number of double bonds per polymer molecule is lowered using the chain transfer agent THF.

The dependence of the double bonds on the number of the polymer molecules is found experimentally to be linear in a first approximation. Figure 4 represents the experimental values compared with the theoretical function $D = P - 0.5I$. In the theoretical function the number of initiator radicals per unit weight of polymer (I) is set constant at 2×10^{-6} mol of initator radicals per g PVC, which according to our experience of VC polymerizations in larger reactors (compare Experimental) is the minimum value for VC polymerization. The experimental results for the nonmodified PVC samples correspond to the theoretical function at low polymerization temperatures (30-50°C) but tend to give lower double bond contents at higher polymerization temperatures. This deviation from theory to lower double bond contents at higher polymerization temperatures can be explained by the assumption that not only the rate of chain transfer but also the rate of termination reaction increases on increasing the polymerization temperature. The presence of THF in VC-polymerization reduces the slope of the linear correlation of the double bonds with the polymer molecules. The number of polymer molecules is increased by additional chain transfer to THF. But the number of double bonds per unit weight of polymer remains the same (within experimental error limits) as the value of the nonmodified PVC sample at the same polymerization temperature. The chain transfer to THF does not result in terminal double bonds, indicating that the migration of a hydrogen atom from THF to the polymer radical is the preferred mechanism of this additional chain transfer.

The proportionality of double bonds in PVC to the number of polymer molecules and their dependence only on the polymerization temperature support the theory that the chain transfer to monomer and possibly the termination reaction are coupled with the formation of terminal double bonds.

IDENTIFICATION OF THE DOUBLE BOND ABSORPTION IN THE IR SPECTRUM OF PVC

The identification of the double bond absorption in the IR spectrum of PVC can be achieved by the correlation of the band intensities with the double bond contents which have been determined using the Wijs reaction. Evaluating in this manner the FTIR spectra of PVC samples (Nos. 3-8) polymerized at different temperatures (compare Tables 2 and 3), the stretching vibration of the double bond is detected at 1667 cm^{-1} (ϵ = 12 L/mol·cm). The correlation of the double bond content with the intensity of the absorption band at 1667 cm^{-1} is demonstrated in Fig. 5. As a measure of the band intensity the quotient of band height (h) and sample thickness (d) is used.

Figure 6 shows some exemplary FTIR spectra of PVC (Nos. 3, 6, and 8) in the characteristic range of wave numbers.

In order to investigate the structure of double bonds in high molecular weight PVC, the stretching vibration at 1667 cm^{-1} has been compared to those of model compounds with a 1-chloro-2-alkene structure, which is the structure of double bonds in low molecular weight PVC [8, 11] (Structure d in Fig. 1). The wave numbers of the double bond stretching vibrations of the model compounds are listed in Table 4.

The double bond stretching vibrations of the trans-1-chloro-2-alkenes are observed in the range from 1663 to 1670 cm^{-1}. This supports the assumption that terminal double bonds with a 1-chloro-2-alkene structure are also present in high molecular weight PVC.

CONCLUSION

The determination of double bonds in PVC can be achieved with high accuracy and in a simple way by the Wijs reaction. Double bonds in PVC are found to be proportional to the number of polymer molecules. The number of double bonds per polymer molecule is always smaller than one. These results support the theory that the chain

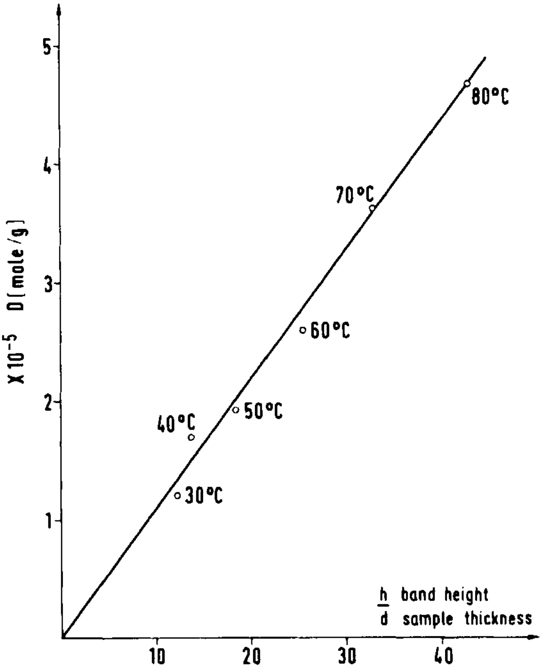

FIG. 5. Correlation of the double bond content (D) with the intensity of the IR-absorption band at 1667 cm^{-1} (h/d).

transfer to monomer and possibly the termination reaction are coupled with the formation of terminal double bonds. Internal double bonds, formed by dehydrochlorination of polymer during polymerization, were excluded by investigating the $Cl^{\ominus}$ content of the water phase of VC suspension polymerization. By the correlation of the double bond content, determined by the Wijs reaction, with the band intensities in the IR spectrum of PVC, the stretching vibration of the PVC double bond was identified at 1667 cm^{-1}. In the same range of wave numbers the stretching vibrations of double bonds in model compounds with a 1-chloro-2-alkene structure are observed, which is the structure of the double bonds in low molecular weight PVC [8, 11]. This comparison supports the assumption that terminal double bonds with a 1-chloro-2-alkene structure are also present in high molecular weight PVC.

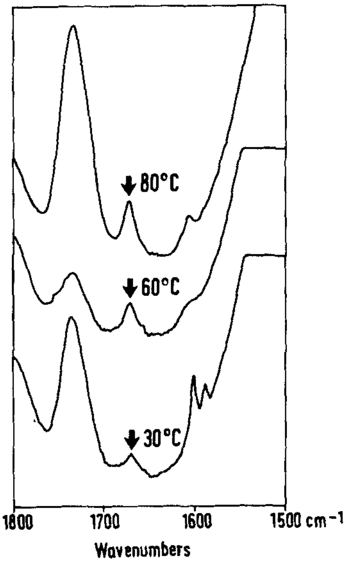

FIG. 6. FTIR spectra of PVC samples Nos. 3, 6, and 8.

TABLE 4

Model compound	Stretching vibration of the double bond (cm^{-1})	Refs.
trans-1-Chloro-2-butene	1670	27
	1667	28
cis-1-Chloro-2-butene	1660	27
1,4-Dichloro-2-butene	1667	29
trans-1-Chloro-2-pentene	1663	27
cis-1-Chloro-2-pentene	1650	27

EXPERIMENTAL

VC Polymerizations Nos. 1 and 2

A 55-L autoclave is charged with 17 kg deionized water, 7 g of a partially hydrolyzed polyvinyl acetate, 5 g methylhydroxypropyl cellulose, 4 g trimethylpentylphenoxy-peracetate, and 4 g t-butyl perneodecanoate. For Polymerization No. 1 the gas phase is left consisting of air after charging. To exclude oxygen in Polymerization No. 2, the charge is purged 10 times with 7.5 bar nitrogen. After the addition of 10 kg VC, the temperature is increased to 50°C. Stirring is done by an impeller at 300 rpm. The polymerization is stopped by degasing when the pressure drops to 1.5 bar below maximum pressure. Degasing is continued under vacuum at 80°C for 1 h. Samples (50 mL) of the water phase are taken before heating to polymerization temperature, during polymerization, and after degasing.

VC Polymerizations Nos. 3-13

A 2-L autoclave equipped with an impeller stirrer (1500 rpm) is used. The charge consists of 882 g deionized water, 1 g methylhydroxypropyl cellulose, 36.3 g THF in the modified polymerizations, initiator(s) as shown in Table 2, and 518 g VC. Before adding VC, oxygen is excluded by purging 10 times with 7.5 bar nitrogen. The polymerization temperature is adjusted to the value given in Table 2. Degasing is begun after the pressure drop has reached 2 bar or the polymerization time exceeds 7.3 h. The degasing temperatures are the polymerization temperatures. To remove residual VC, the suspensions are treated for 1 h by heating to 80°C under vacuum.

Determination of Double Bond Content by Wijs Reaction

The solution of 2 g PVC in 200 mL 1,2-dichloroethane is reacted with 60 mL of an approximately 1 M solution of iodine monochloride in trichloromethane (160 g ICl_3 and 180 g I_2 in 2 L $CHCl_3$). The reaction mixture is stirred at room temperature for 15 min and then poured into 5 L methanol. Excess iodine monochloride is removed by decanting the methanol from the precipitated polymer, suspending the polymer in 5 L methanol and decanting, and repeatedly suspending and washing the polymer with methanol (500 mL) till a colorless filtrate is obtained. The polymer is dried under vacuum at maximum 40°C and then pressed with 150 bar at room temperature to a tablet form. Determination of the iodine content in the prepared sample is done by x-ray fluorescence analysis in the usual way.

Determination of Molecular Weight by GPC

A combination of columns with the exclusion limits 2×10^3, 5×10^3, 1×10^4, and 7×10^4 nm is used, which had been calibrated using narrowly distributed fractions of polystyrene. Samples are prepared by heating the solution of 0.5% PVC in THF at 120°C for 1 h to destroy associates followed by chilling using a Dry Ice/acetone mixture. Two milliliters of this solution are injected and then eluted at 23°C at a rate of 1 mL THF per minute.

Determination of $Cl^{\ominus}$ Ions in Water Phase

The samples taken during VC polymerization are filtered. Then acetone is added to the water phase to reduce the solubility of AgCl during the titration of $Cl^{\ominus}$ ions with n/100 $AgNO_3$. The titration is followed potentiometrically.

Precipitation of PVC

Two grams PVC are dissolved in 200 mL 1,2-dichloroethane by heating to a maximum of 60°C in a closed vessel. This solution is added to 1 L methanol with stirring. The precipitated polymer is filtered and then dried under vacuum at maximum 40°C.

IR Spectrum of PVC

PVC precipitated from 1,2-dichloroethane is pressed with 200 bar at room temperature to films of 600 to 1000 μm thickness. FTIR spectra are taken of these films by a Digilab 15 B/D or 15 C.

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