

## The NORDFORSK PVC Polymer Characterization Project

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### Synopsis

Nordic research and industrial laboratories under the auspices of NORDFORSK performed a series of round-robin tests on characterization methods for PVC. Ten samples of commercial-type emulsion and suspension PVC were used. The resins covered a broad range of molecular weight. Gel permeation chromatography (GPC) was used to determine molecular weight distribution and molecular weight averages,  $\bar{M}_n$  and  $\bar{M}_w$ . These were also determined by osmometry and light scattering measurements, respectively. A good correlation was found for these three methods but GPC was by far the most versatile. Intrinsic viscosity was determined and viscometric routine analysis were investigated to evaluate the precision and informative value of such analysis. Solution viscometry according to the ISO or DIN standard proved to be quite adequate, being accurate, fast, versatile, and inexpensive. NMR spectroscopy was found to be much more accurate for quantitative tacticity determinations than infrared or Raman spectroscopy. For most characterization methods, remarkably good agreement between the laboratories was reached. The thorough investigations of the methods used resulted in detailed recommendations for viscometric, osmometric, and GPC determinations.

### INTRODUCTION

In the year 1969, representatives of research and industrial laboratories from the Nordic countries (Denmark, Finland, Norway, and Sweden) came together under the auspices of NORDFORSK (Scandinavian Council for Applied Research) to start a common project concerning structure and properties of industrially important synthetic polymers. In connection with this project, a subgroup, NORDFORSK Polymer Characterization Group, was formed with the aim of studying characterization methods important to current industrial activities and academic research in the Nordic countries. The work was first directed toward poly(vinyl chloride) (PVC) and polyethylene (PE).

In this report, the work on PVC during the years 1970-1973 is summarized. It involves the determination of molecular weight distribution MWD, molecular weight averages  $\bar{M}_n$  and  $\bar{M}_w$ , intrinsic viscosity  $[\eta]$ , and tacticity. Besides these determinations used in scientific work, viscometric routine analysis was investigated in order to evaluate the precision and informative value of such analysis and to find out whether alternative procedures could be suggested. A further object of these investigations was to characterize a set of batches of PVC resins useful in other NORDFORSK research activities.

A series of round robin tests was carried out involving steps of successive refinements in the measuring technique. During the work, three different sets of PVC resins were characterized, totaling ten resins. The results were discussed at eight meetings. Detailed recommendations have been worked out for viscometric, osmometric, and gel-chromatographic (GPC) determinations on PVC. These recommendations were intended to be published separately. Due to changes in the policy of NORDFORSK, this work had to be canceled. Nor could the other plans for cooperative work within the group be carried through.

## EXPERIMENTAL AND RESULTS

### Characterization Methods, Samples, and Investigators

The participating laboratories and the methods used are listed in Table I. The PVC resins used are listed in Table II. They include suspension- and emulsion-polymerized resins of commercial and experimental type. The polymers are grouped according to the order in which they were investigated.

In the first round, the work concerned one commercially available standard quality suspension resin and one research quality emulsion resin of similar molecular weight. These polymers were kindly supplied by Dr. H. Leth-Pedersen (A/S Nordiske Kabel- og Traadfabrikker, Kemisk Forskningslaboratorium, La Coursvej 7, DK-2000 Copenhagen, Denmark) and Prof. J. Ugelstad (SINTEF, N-7034 Trondheim-NTH, Norway), respectively. During the NORDFORSK work, they stored an appropriate quantity of respective polymer batches.

In the second round, a series of suspension and emulsion polymers with three different levels of molecular weight was investigated. The material, one commercial and five experimental polymers, was kindly delivered by KemaNord AB (Fack, S-850 13 Sundsvall, Sweden) and Norsk Hydro A/S (Porsgrunn Fabrikker, N-3901 Porsgrunn, Norway) in close cooperation. The experimental polymers were produced in pilot plant quantities exclusively for this investigation. Typical standard procedures for suspension and emulsion polymerization were followed (see Appendices 1 and 2). Changes in molecular weight were achieved by changes in polymerization temperature (PT).

In the third round, some of the recommended characterization procedures were tested on two commercial suspension polymers of similar molecular weight. The resins were kindly supplied by Norsk Hydro A/S and KemaNord AB, respectively. During the NORDFORSK work, samples of group 2 and 3 resins could be ordered from these companies.

### Solvents and Dissolution Methods

Tetrahydrofuran (THF), purum, and cyclohexanone (CH) were used as solvents throughout the investigation. A few tests with dimethylformamide (DMF) and dimethylacetamide (DMA) gave inconsistent results, as expected.

Retention of molecular aggregates of PVC even in good solvents is well known and has been studied elsewhere (see, for example, Andersson et al.<sup>1</sup>) As confirmed in this investigation, the presence of aggregates will noticeably influence GPC and light-scattering (LS) measurements but not osmometric or viscometric measurements.

TABLE I  
Participating Laboratories and Method Used

	$\bar{M}_n$ (osmom.)	$\bar{M}_w$ (LS)	$\bar{M}_n, \bar{M}_w$ , MWD		$[\eta]$ $\eta_{rel}$ (viscometry)	Tacticity		
			(GPC)	(GPC)		Raman	IR	NMR
1. Danmarks Tekniske Højskole, Sect. of Polymer Technology, Lyngby, Denmark	x	-	x	x	x	-	-	-
2. Nordisk Kabel-og Traadfabriker, København, Denmark	x	x	x	x	-	-	-	-
3. Dept. of Wood and Polymer Chemistry, Univ. of Helsinki, Finland	x	-	-	x	-	x	x	x
4. Neste OY, Kullo, Finland	x	x	x	-	-	-	-	x
5. Finnish Pulp and Paper Research Institute, Tapiola, Finland	-	x	-	-	-	-	-	-
6. Pekema OY, Kullo, Finland	-	-	-	-	x	-	-	-
7. Norsk Hydro A/S, Forsgrunn, Norway	-	-	-	-	x	-	-	-
8. SINTEF, Trondheim, Norway	x	-	-	-	-	-	-	-
9. Chalmers Tekniska Högskola, Polymergruppen Göteborg, Sweden	-	-	x	x	x	x	x	x
10. KemaNord AB, Sundsvall, Sweden	-	-	-	-	-	-	-	-
11. L.M. Ericsson AB, Stockholm, Sweden	-	-	x	-	x	-	-	-

TABLE II  
 Investigated PVC Resins

Chronologic group	Designation	Polymerization		K value <sup>b</sup>	Delivered by
		System <sup>a</sup>	Temp, °C		
1.	Corvic D65/8,	S	—	65	Dr. H. Leth-Pedersen, NKT
	X-AB	E <sub>expt</sub>	—		
2.	S-54	S <sub>expt</sub>	75	53.1	Prof. J. Ugelstad, SINTEF
	Pevikon R-24 <sup>c</sup>	S	55	66.5	KemaNord AB
	S-80	S <sub>expt</sub>	43	78.6	KemaNord AB
	E-54	E <sub>expt</sub>	75	54.6	Norsk Hydro A/S
	E-67	E <sub>expt</sub>	57	68.7	Norsk Hydro A/S
	E-80	E <sub>expt</sub>	43	81.2	Norsk Hydro A/S
3.	Pevikon S-685	S	—	68	KemaNord AB
	Norvinyl S9-70	S	—	68	Norsk Hydro A/S

<sup>a</sup> E = Emulsion polymerization; S = suspension polymerization, expt = experimental quality.

<sup>b</sup> K value according to Fikentscher reported by supplier.

<sup>c</sup> Present designation of this resin type: Pevikon S-657.

In order to disintegrate PVC aggregates in THF solutions, autoclaving for 3 hr at 120°C is recommended.<sup>2</sup> An inexpensive autoclave specially designed for this purpose has been constructed. Drawings and autoclaves may be ordered from Chalmers University of Technology (Chalmers University of Technology, Polymer Group, Fack, S-402 20 Gothenburg, Sweden).

As a safety precaution, peroxides should be removed from THF by refluxing over sodium borohydride followed by distillation over sodium.<sup>1</sup> The solvent and solutions should be kept under nitrogen. Presence of peroxides may influence spectrometric determinations on PVC obtained from THF solutions but does not seem to influence the other determinations investigated.

### Light Scattering (LS)

Absolute determinations of  $\bar{M}_w$  were performed by LS at 5460 Å of THF and CH solutions at 20–25°C. The THF solutions were autoclaved 2 hr at 120°C. The results and further experimental details are given in Table III. Values from the same laboratory using the same technique are given in the same row in the table even when the measurements were performed on different occasions. However, when different techniques were used, the data are given in separate rows. This method of presentation is used throughout the report if not otherwise stated.

As rather few LS measurements were undertaken, few statements can be made. At the most, one resin, Corvic D65/8, was investigated by four laboratories. In this case the coefficient of variation between the mean  $\bar{M}_w$  values is only 2.0%. Measurements on CH and THF solutions show reasonable agreement whenever comparison is possible, i.e., for Corvic D65/8, X-AB, and Pevikon R24. No differences between results from various measuring equipment are observable. It might be concluded that the LS measurements on CH and THF solutions of PVC were more easy to perform and gave more conformity of results than expected.

### Membrane Osmometry

Absolute determinations of  $\bar{M}_n$  were performed with high-speed automatic membrane osmometers using CH and DMF solutions.

Experimental details and results are given in Table IV. DMF proved to be a bad solvent compared with CH. Membranes of the type Sartorius SM 11539 and Schleicher & Schüll 08 gave equivalent results, while Sartorius SM 11536 was too permeable for low molecular weight species. This explains the high  $\bar{M}_n$  values given in the last row of the table. Apart from these results, the measurements show excellent agreement. For Corvic D65/8, the coefficient of variation for the  $\bar{M}_n$  determinations at four laboratories is 5.1%. No difference between different measuring equipment is observed.

### Determination of $\theta$ Temperature

A special investigation concerning the determination of the  $\theta$  temperature was undertaken at the University of Helsinki. The Flory  $\theta$  temperature is an important thermodynamic quantity which may, in principle, be determined by

TABLE III  
Results Obtained by Light Scattering ( $\bar{M}_w \times 10^{-3}$ )<sup>a</sup>

Corvic D65/8	Pevikon				E-54	E-67	E-80	Solution	dn/dc, ml/g	Remarks
	X-AB	S-54	R-24	S-80						
103.3	96.8		83.6				CH	0.074	SOFICA-40B	
106.0 <sup>b</sup>							THF	0.1108	SOFICA-4200	
107.0	101.0						THF	0.107	Brice-Phoenix-2000	
108.0	118.0									
		43.6			44.5	99.0	THF	0.1065	SOFICA-40B	
Average	105.3	43.6	104.0	124.5	44.5	99.0	THF	0.109	Brice-Phoenix-2000	
106.0				124.5						

<sup>a</sup> All measurements at ambient temperatures.

<sup>b</sup> Extrapolation to zero angle from constant  $C/R_\theta$  values.

TABLE IV  
Results Obtained by Osmometry ( $\bar{M}_n \times 10^{-3}$ )

Corvic D65/8	Pevikon				E-54	E-67	E-80	Pevikon S-685	Norvinyl S9-70	Solvent, measuring temp., °C, and membrane type
	X-AB	S-54	R-24	S-80						
49.5	27.2	41.9	73.1	28.5	50.2	67.4	45.7	44.6	CH	35 Sartorius SM 11539
54.0	26.0	44.8	71.2	28.7	45.6	68.5	48.8	49.6	CH	25 Sartorius SM 11539
49.0	53.6			29.0	43.9	69.0			CH	35 Schleicher & Schüll 08
53.5	49.1	43.4	69.1	34.8	51.0	67.0			CH	35 Schleicher & Schüll 08
Average	51.5	43.3	71.1	30.3	47.7	68.0	47.3	47.1	CH	35 Sartorius SM 11539
75.6	58.7									
67.7	60.9	33.0	80.9	31.8	50.1	86.2			DMF	25 Sartorius SM 11536
									DMF	25 Sartorius SM 11536
									CH	25 Sartorius SM 11536

TABLE V  
First Virial Coefficient  $A_1$ , Second Virial Coefficient  $A_2$ , and Flory's Theta  
Temperature  $\theta$  for PVC in Cyclohexanone Determined by Membrane Osmometry at  
308–322°K (35–49°C) Using Sartorius SM 11539 Membranes

Parameter	Pevikon					
	S-54	R-24	S-80	E-54	E-67	E-80
$A_1 \times 10^5$	3.534	2.309	1.408	3.300	2.096	1.471
$A_2$ , mole·cm <sup>3</sup> /g <sup>2</sup>						
308°K	2.306	3.322	1.989	2.293	1.058	2.307
311°K	3.979	—	—	3.567	3.508	—
315°K	4.989	4.753	2.461	5.055	4.040	2.723
322°K	—	5.758	(2.473)	—	—	3.492
$\theta$ , °K	302	288	282	303	306	291

osmometric measurements.<sup>3</sup> In polymer solutions at  $T = \theta$  ( $\theta$  conditions), the polymer chain dimensions are unperturbed by intramolecular interactions. Measurements on polymer solutions at  $\theta$  are ideal from a thermodynamic point of view. Thus, theory predicts  $\alpha$  in the Mark-Houwink equation,

$$[\eta] = K_{\theta} \bar{M}_w^{\alpha}$$

to be 0.5, independent of polymer and solvent type.  $K_{\theta}$  should be nearly independent of the solvent type. From theoretical considerations, Van Krevelen and Hoftyzer<sup>4</sup> have estimated the  $K_{\theta}$  value of PVC to be  $12.4 \times 10^{-4}$ .

An estimate of  $\theta$  may theoretically be determined from the temperature dependence of the second virial coefficient,  $A_2$ , by extrapolating  $A_2$  to zero.  $A_2$  is given by the virial equation for osmotic pressure,

$$\frac{\Pi}{CRT} = A_1 + A_2 \cdot C + \dots$$

where  $A_1, A_2 \dots$  are virial coefficients,  $C$  is solute concentration, and  $\Pi$  is osmotic pressure.

To test this seemingly simple method, a separate series of measurements on "group 2 resins" in CH was utilized for a calculation (see Table V).  $A_1$  was taken as the reciprocal of  $(\bar{M}_n)_{\text{average}}$ , Table IV. The data of Table V indicate that the scatter of the  $A_2$  values is quite high. This adversely affects the estimate of  $\theta$ . A definite trend toward lower  $\theta$  values with increasing molecular weight (lower PT) is indicated.

The scatter in  $A_2$  will not influence the calculated average value of  $\theta$  to a great extent, however. The  $\theta_{\text{calculated}}$  was found to be  $295^{\circ} \pm 12^{\circ}\text{K}$  for the samples investigated. This is apparently too high a value. A  $\theta$  temperature around  $295^{\circ}\text{K}$  for the PVC/CH system implies that ordinary viscometric and osmometric determinations on PVC at room temperature would be carried out near  $\theta$  conditions. This is not in accordance with general experience, which can be seen, e.g., by comparing the theoretical values of  $\alpha$  and  $K_{\theta}$  given above with experimentally found values: Theoretical values:  $\alpha = 0.5$ ,  $K_{\theta} = 12.4 \times 10^{-4}$ . Experimental values<sup>5</sup> in CH at  $25^{\circ}\text{C}$ :  $\alpha = 0.78$ ,  $K = 1.38 \times 10^{-4}$ .

The reason why such a high value for the  $\theta$  temperature was obtained in this case is not fully understood. In fact, a  $\theta$  temperature of  $303^{\circ}\text{K}$  is reported<sup>6</sup> for PVC. This may well be correct, however, as it refers to the system THF–water

(100:11.9), which is a commonly used precipitation system for PVC at room temperature.

### Gel Permeation Chromatography (GPC)

Determination of molecular weight distribution (MWD) and molecular weight averages was performed by GPC using a Waters GPC Model 200 and, in one case, a Model Ana-Prep. All participants followed the ordinary experimental procedure recommended by Waters: solvent, THF; temperature, 25°C; sample volume, 2 ml; sample concentration, 2–3 mg/ml; injection time, 2 min; flow rate, 1.0 ml/min; columns, 4–5 Styragel columns, plate count > 700 plates/ft, range  $10^3$ – $10^5$  Å or higher.

During the work, some laboratories changed their column combinations in order to increase the resolution in the high molecular weight part of the MWD. The need for heat treatment of the sample solutions (3 hr at 120°C) was also investigated by some workers. Considerable attention was paid to alternative procedures for calibration and data treatment.

#### *Calibration*

In the calibration procedure, all participants used the same narrow-distribution standards of polystyrene (PS) delivered by Waters. Transformation of the relation found for PS between elution volume ( $V_e$ ) and the molecular weight ( $M$ ) into a calibration curve for PVC was performed either by the universal calibration principle<sup>7</sup> or the  $Q$ -factor method.<sup>8</sup>

Most workers preferred the universal calibration method. This implies that the separation in GPC is governed by the hydrodynamic volume of the solute and that  $[\eta]M$  is a measure of the hydrodynamic volume. The Mark–Houwink equation relates  $[\eta]$  to  $M$  for flexible, unbranched polymers and thus provides a simple means to convert a PS calibration into a PVC calibration. Most workers used the relations<sup>9</sup>

$$[\eta]_{\text{PS}} = 1.179 \times 10^{-4} \bar{M}_w^{0.72}$$

$$[\eta]_{\text{PVC}} = 1.35 \times 10^{-4} \bar{M}_w^{0.77}$$

One laboratory used a slightly different equation for PVC<sup>5</sup>:

$$[\eta]_{\text{PVC}} = 1.5 \times 10^{-4} \bar{M}_w^{0.77}$$

This laboratory also measured  $[\eta]$  directly for the PS standards used. It turned out that these two approaches gave about the same GPC results.

A few workers used the  $Q$ -factor method. This is based on the assumption that separation in GPC is related to the extended chain length of the solute molecules. Although this assumption is not generally valid, the results confirm that the method may be used for unbranched, undegraded PVC (see Table VI and ref. 9).

#### *GPC Data Treatment*

The GPC curves for all samples were quite similar in shape, showing the regular, fairly narrow distribution characteristic for undegraded PVC. Computing



TABLE VI  
Comparison Between Universal Calibration Principle (*U*) and *Q*-Factor Method (*Q*)<sup>a</sup>

	Corvic D65/8		Pevikon						
			S-54	R-24	S-80	E-54	E-67	E-80	
$\overline{M}_nU \times 10^{-3}$	52.2	51.7	53.1	26.1	40.7	50.6	26.7	42.4	54.2
$\overline{M}_nQ \times 10^{-3}$	46.0	47.5	48.5	23.4	36.8	44.8	23.6	38.7	48.5
$\overline{M}_nU/\overline{M}_nQ$	1.13	1.09	1.09	1.12	1.11	1.13	1.13	1.10	1.12
$\overline{M}_wU \times 10^{-3}$	122.0	115.0	117.0	53.2	86.2	127.0	56.7	97.4	146.0
$\overline{M}_wQ \times 10^{-3}$	113.0	108.5	109.0	47.2	77.6	117.0	50.6	89.8	135.0
$\overline{M}_wU/\overline{M}_wQ$	1.08	1.06	1.08	1.13	1.11	1.09	1.12	1.08	1.08

<sup>a</sup> Corvic D65/8 measured with three different column combinations. All other samples analyzed with still another column combination.

MWD and molecular weight averages from the GPC curves was performed according to Waters recommendations using different computer facilities. The difference in results when using two well-known computer programs on the same experimental data is illustrated in Table VII. Drott's program allows for the calculation of long-chain branching if values of the intrinsic viscosity are included.

In Waters recommendations, no correction for axial dispersion is included. Calculations have shown that the gain in precision is of importance only for narrow distributions but not when  $\overline{M}_w/\overline{M}_n > 2$ . There is also a considerable risk for introducing errors when using these corrections. Our results clearly illustrate these different aspects: After correction,  $\overline{M}_n$  should increase and  $\overline{M}_w$  decrease. In Table VIII, examples of the effect of unintentionally introduced errors are given. In another investigation, Table IX, using the same data program, the corrections were in the proper direction but quite insignificant compared with the experimental errors.

### Reproducibility

The reproducibility of the GPC measurements is quite good. The coefficient of variation within a single laboratory using standardized technique was 2–6% over an extended period of time (Table X). Between the participating laboratories, the variation was also very small although the samples represented different polymerization systems and molecular weight ranges. This is still more remarkable because different pretreatments of the sample solutions were used as well as different methods for GPC calibration (Table XI). In fact, the results

TABLE VII  
Comparison Between Results Obtained When Using Different Computer Programs on the Same Experimental GPC Data

	Program	$\overline{M}_n \times 10^{-3}$	$\overline{M}_w \times 10^{-3}$
Pevikon S-685	Drott <sup>a</sup>	44.8	91.8
	Pickett <sup>b</sup>	46.0	96.5
Norvinyl S9-70	Drott <sup>a</sup>	43.9	95.2
	Pickett <sup>b</sup>	45.0	99.6

<sup>a</sup> E. E. Drott and R. A. Mendelson, *J. Polym. Sci. A-2*, **8**, 1361 and 1373 (1970).

<sup>b</sup> H. E. Pickett, M. J. R. Cantow, and J. F. Johnson, *J. Appl. Polym. Sci.*, **10**, 917 (1966).

are much more uniform in this round robin test than in the IUPAC round<sup>10</sup> performed in 1969. This is an effect of the close cooperation between the Nordic laboratories made possible by the active work in the NORDFORSK Polymer Characterization Group.

TABLE VIII  
Erratic Influences of Correction for Axial Dispersion on GPC Data<sup>a</sup>

	Pevikon					Pevikon Norvinyl		
	S-54	R-24	S-80	E-54	E-67	E-80	S-685	S9-70
$\bar{M}_n$ uncorr. $\times 10^{-3}$	26.1	40.7	50.6	26.7	42.4	54.2	44.8	43.9
$\bar{M}_n$ corr. $\times 10^{-3}$	29.1	47.0	59.7	29.9	49.1	64.3	38.8	44.1
$\bar{M}_w$ uncorr. $\times 10^{-3}$	53.2	86.2	127.0	56.9	97.4	146.0	91.8	95.2
$\bar{M}_w$ corr. $\times 10^{-3}$	54.1	88.6	134.0	57.6	100.0	153.0	83.6	89.6

<sup>a</sup> For Pevikon S-685 and Norvinyl S9-70, the correction method and data program used were according to S. T. Balke and A. E. Hamielec, 6th Int. Seminar on GPC, Miami Beach, Oct. 1968. For all other samples, the correction procedure applied was according to S. T. Balke and A. E. Hamielec, *J. Appl. Polym. Sci.*, 13, 1381 (1969).

TABLE IX  
Expected Influence of Correction for Axial Dispersion on GPC-Data  
Sample: Corvic D65/8. Correction program used: S. T. Balke and A. E. Hamielec,  
6th Int. Seminar on GPC, Miami Beach, Oct. 1968. (Compare Table VIII.)  
Three different column combinations were used.

Column combination	A	B	C
$\bar{M}_n$ uncorr. $\times 10^{-3}$	52.2	51.7	52.7
$\bar{M}_n$ corr. $\times 10^{-3}$	52.3	51.7	53.5
$\bar{M}_w$ uncorr. $\times 10^{-3}$	122.0	115.0	120.0
$\bar{M}_w$ corr. $\times 10^{-3}$	112.0	108.0	109.0

Remark: Column combination A:  $3 \times 10^5$ ,  $1 \times 10^5$ ,  $3 \times 10^4$ ,  $1.5 \times 10^4$  A

Remark: Column combination B:  $1 \times 10^6$ ,  $3 \times 10^5$ ,  $1 \times 10^5$ ,  $3 \times 10^4$ ,  $1.5 \times 10^4$  A

Remark: Column combination C:  $1 \times 10^6$ ,  $2 \times 10^4$ ,  $1 \times 10^4$ ,  $1 \times 10^3$  A

TABLE X  
Reproducibility of GPC Measurements Within One Laboratory<sup>a</sup>

Solution pretreatment	Date of test	$\bar{M}_n \times 10^{-3}$	$\bar{M}_w \times 10^{-3}$	$\bar{M}_z \times 10^{-3}$
—	5/29/70	49.3	118.4	249.4
—	6/30/70	45.9	116.5	238.2
—	10/5/70	42.3	113.8	220.5
—	10/8/70	45.4	115.6	227.6
	Average	45.7	116.1	233.9
	Coeff. of var., %	6.3	1.6	5.4
120°C, 2 h	6/1/70	44.2	109.3	195.9
120°C, 3 h	9/21/70	45.1	113.4	205.3
120°C, 3 h	10/5/70	46.6	111.5	202.2
120°C, 3 h	10/7/70	45.4	111.3	202.2
	Average	45.3	111.4	201.4
	Coeff. of var., %	2.2	1.5	2.0

<sup>a</sup> Sample: Corvic D65/8.

TABLE XI  
 Reproducibility of GPC Measurements Among Different Laboratories. Autoclaved and Nonautoclaved Solutions.  
 Calibration According to Universal Calibration Procedure or Q-Factor Method

	Corvic		Pevikon			Pevikon			Norvinyl	
	D65/8	X-AB	S-54	R-24	S-80	E-54	E-67	E-80	S-685	S9-70
$\bar{M}_n \times 10^{-3}$	—	—	26.1	40.7	50.6	26.7	42.4	54.2	41.0	41.8
	53.5	47.0	26.4	44.7	61.7	30.8	47.2	67.5	44.0	47.0
	—	—	26.1	49.3	61.4	27.5	39.2	72.0	42.3	44.7
	45.3	47.1	26.5	39.8	57.3	26.8	42.4	57.7	46.0	45.0
	50.2	52.3	26.1	43.3	59.4	27.2	43.7	63.1	47.5	50.0
	49.7	48.8	26.2	43.6	58.1	27.8	42.9	62.9	44.2	45.7
Average	8.3	6.2	0.7	8.6	7.8	6.1	6.0	11.5	6.0	6.6
Coeff. of var., %	—	—	53.2	86.2	127.0	56.7	97.4	146.0	93.3	96.0
$\bar{M}_w \times 10^3$	115.0	113.4	48.7	82.7	133.8	54.9	97.4	153.5	98.0	101.3
	—	—	57.2	104.2	161.1	63.2	111.1	183.1	91.1	91.0
	111.4	108.3	51.2	89.5	143.0	57.7	99.1	162.4	96.5	99.6
	106.1	115.9	53.3	91.6	142.9	57.4	99.5	166.5	101.1	104.3
Average	110.8	112.5	52.7	90.6	141.6	58.0	100.9	162.3	96.0	98.4
Coeff. of var., %	4.0	3.4	5.9	8.1	9.1	5.4	5.7	8.7	4.1	5.2

TABLE XII  
Effect of Heat Treatment (3 h, 120°C) of Sample Solutions on GPC Measurements

	$\bar{M}_n \times 10^{-3}$		$\bar{M}_w \times 10^{-3}$	
	Nonautocl.	Autocl.	Nonautocl.	Autocl.
Corvic D65/8	45.7	45.3	116.1	111.4
	49.9	53.5	118.7	115.0
	49.7	50.2	106.3	106.1
X-AB	46.0	47.1	120.7	108.3
S-54	26.6	26.1	54.0	53.2
	24.8	22.7	51.2	48.4
	49.2	49.3	104.2	104.7
Pevikon R-24	40.0	40.7	89.2	86.2
	42.1	39.3	87.7	82.7
	55.1	50.6	144.0	127.0
S-80	55.5	54.9	139.9	133.8
	27.2	26.7	57.2	56.7
E-54	26.4	26.8	57.2	54.9
	43.4	42.4	105.0	97.4
E-67	40.1	41.6	94.5	97.4
	58.0	54.2	175.0	146.0
E-80	63.8	60.1	151.0	153.5

### Column Combination and Resolution

As pointed out earlier, the column combination should be chosen in such a way that a good resolution is obtained within the molecular weight range of interest. The  $\bar{M}_w$  values of group 2 resins, row 3 Table XI, illustrates the effect of inferior resolution in the high molecular weight part of the MWD. In the subsequent testing round, an improved column combination was used (see group 3 resins, row 3, Table XI). On the other hand, as shown in Table IX, there is little reason to further improve an already acceptable resolution.

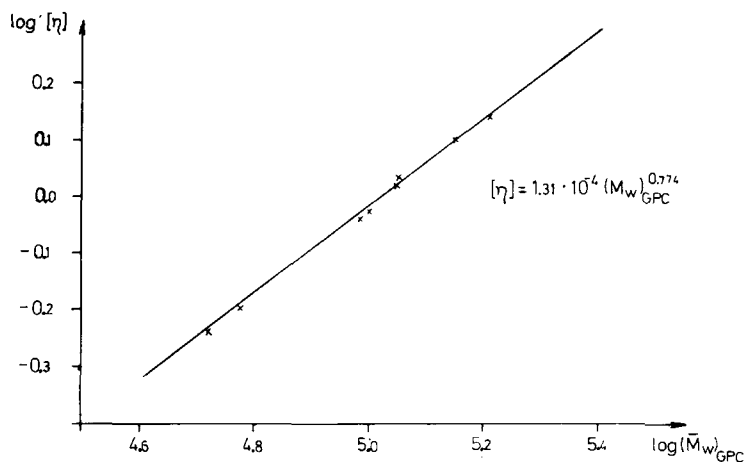


Fig. 1. Relation between  $[\eta]_{\text{THF}}^{25^\circ\text{C}}$  and  $(\bar{M}_w)_{\text{GPC}}$ .

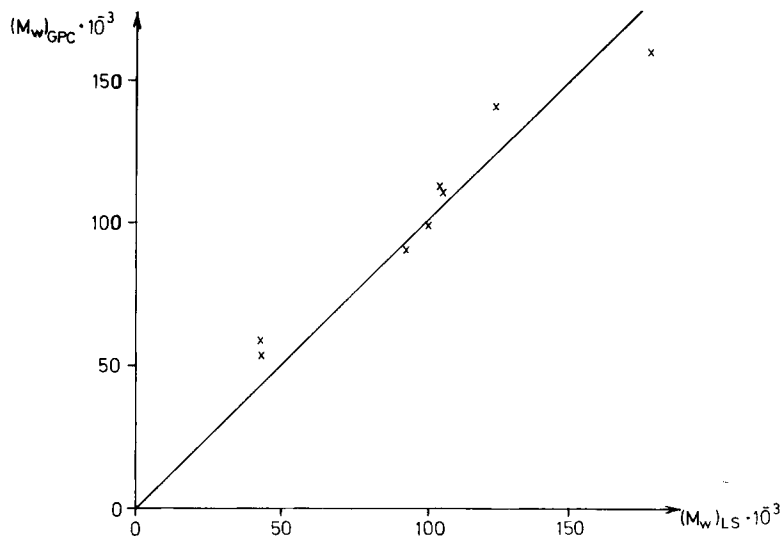


Fig. 2. Comparison between  $\bar{M}_w$  values obtained by LS and GPC. Solid line represent  $(\bar{M}_w)_{\text{GPC}} = (\bar{M}_w)_{\text{LS}}$ .

### Heat Treatment of Sample Solutions

Retention of molecular aggregates of PVC even in good solvents is well known and has been studied elsewhere.<sup>2,11</sup> This investigation confirms that molecular aggregation influences the GPC measurements (Table XII). For practical purposes, however, heat treatment (3 hr at 120°C) is not necessary for undegraded samples of ordinary commercial PVC, only for high molecular weight resins. Even for such polymers,  $\bar{M}_n$  is hardly influenced (see also Table X). On the other hand, high molecular weight fractions, degraded samples, and samples of high tacticity always call for heat treatment of the sample solutions.<sup>1,2</sup>

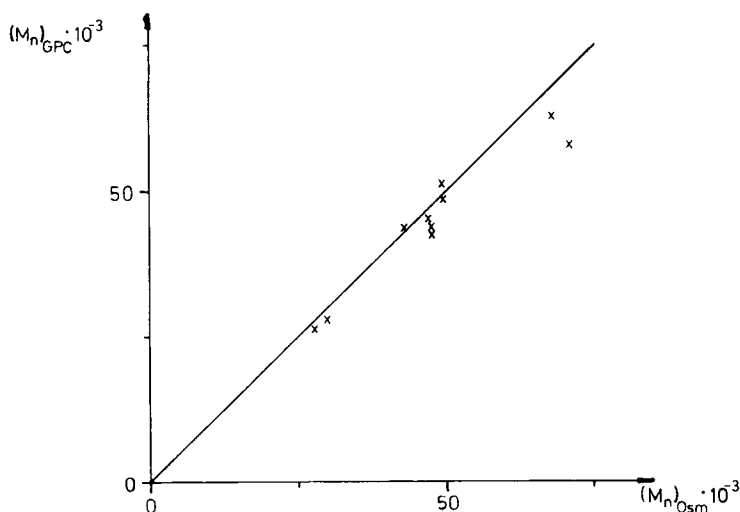


Fig. 3. Comparison between  $\bar{M}_n$  values obtained by osmometry and GPC. Solid line represent  $(\bar{M}_n)_{\text{GPC}} = (\bar{M}_n)_{\text{osm}}$ .

TABLE XIII  
 Viscosity Measurements

PVC resin	[ $\eta$ ]		$\eta_{rel}$	No. <sup>b,c</sup> $\eta_{red}$ <sup>b</sup>	$K^{b,d}$	
	in THF	in CH				
Corvic D65/8	1.05	1.11				
		1.12				
		1.07				
		1.09				
		1.09				
Average	1.05	1.10				
X-AB	1.08	1.16				
		1.08				
		1.09				
		1.01				
		1.08				
Average	1.08	1.08				
S-54	0.66 (corr) <sup>a</sup>	0.63	1.34	68		
		0.58	0.61	1.35	69	
				1.34	68	
				1.35	69	
				1.35	69	
Average	0.58	0.62	1.35	69	53.6	
Pevikon R-24	0.96 (corr) <sup>a</sup>	0.90	1.56	112		
				1.54	108	
				1.56	112	
			0.95			
			0.88			
		0.90				
Average		0.91	1.56	111	66.9	
S-80	1.36 (corr) <sup>a</sup>	1.28	1.84	162		
				1.81	168	
				1.81	162	
				1.81	161	
				1.81	162	
Average		1.26	1.82	165	78.9	
E-54	0.69 (corr) <sup>a</sup>	0.65	1.36	73		
		0.66 (corr) <sup>a</sup>	0.63	1.36	72	
		0.64		1.37	73	
		0.63		1.36	73	
					72	
Average	0.64	0.64	1.36	73	54.3	
E-67	1.02 (corr) <sup>a</sup>	1.00	1.59	118		
		1.06	0.93	1.59	118	
		(0.80)		1.59	117	
				1.60	117	
					119	
Average	1.06	0.97	1.59	118	68.5	
E-80	1.46 (corr) <sup>a</sup>	1.36	1.85	175		
		1.39	1.42	1.88	170	
				1.88	176	
				1.90	175	
					179	
Average	1.39	1.39	1.88	175	81.3	
Pevikon S-685	1.04 (corr) <sup>a</sup>	—	1.59	118		
				1.60	119	
				1.59	117	
				1.60	120	

continued

TABLE XIII

PVC resin	[ $\eta$ ]		$\eta_{rel}$	No. b,c $\eta_{red}^b$	$K^{b,d}$
	in THF	in CH			
Average	1.00		1.60	118	69.0
Norvinyl S9-70	1.04 (corr) <sup>a</sup>	—	1.61	122	
	1.00		1.62	125	
			1.60	120	
			1.61	121	
Average	1.00		1.61	122	69.5

<sup>a</sup> Corrected for kinetic energy loss.

<sup>b</sup> Determined according to ISO standard R 174.

<sup>c</sup> ISO viscosity number =  $\frac{\eta - \eta_0}{\eta_0 \cdot C} = (\eta_{rel} - 1) \frac{1}{C}$  where C = concentration in g/100 ml.

<sup>d</sup> K-value according to H. Fikentscher, *Cellulosechemie*, 13, 58 (1932)

$$\log \eta_{rel} = C \cdot \left[ \frac{75 K^2}{1 + 1.5 KC} + K \right]$$

where C = concentration in g/100 ml.

#### Accuracy of the GPC Data

In Table XI, relevant GPC data of the investigated samples are summarized. The Mark-Houwink relation given in Figure 1 is based on these data and the [ $\eta$ ] values given in Table XIII. This relation,

$$[\eta] = 1.31 \times 10^{-4} (\overline{M}_w)_{GPC}^{0.774}$$

is in excellent agreement with the relation used for the universal calibration procedure<sup>9</sup> (see above). It is a strong indication that the GPC and viscometric measurements have been carried out with great accuracy and precision. Comparing Tables XI, III, and IV show good agreement between GPC, osmometric, and light-scattering measurements. This is also illustrated in Figures 2 and 3.

#### Solution Viscometry

Viscometric measurements were carried out in CH and THF at 25°C using Ubbelohde viscometers and, in one case, Ostwald viscometers. The bulk of the investigations was carried out according to the ISO standard R 174, i.e., determining  $\eta_{rel}$  at a concentration of 0.005 g/ml in CH. Intrinsic viscosity was also determined. The results are summarized in Table XIII.

The viscometric determinations show an extraordinarily good agreement between the different laboratories. Furthermore, there are virtually no differences between CH and THF in these measurements, irrespective of concentration and molecular weight. The results of the viscometric measurements according to the ISO standard are given in three ways, which, in fact, are equivalent: Relative viscosity:

$$\eta_{rel} = \eta/\eta_0$$

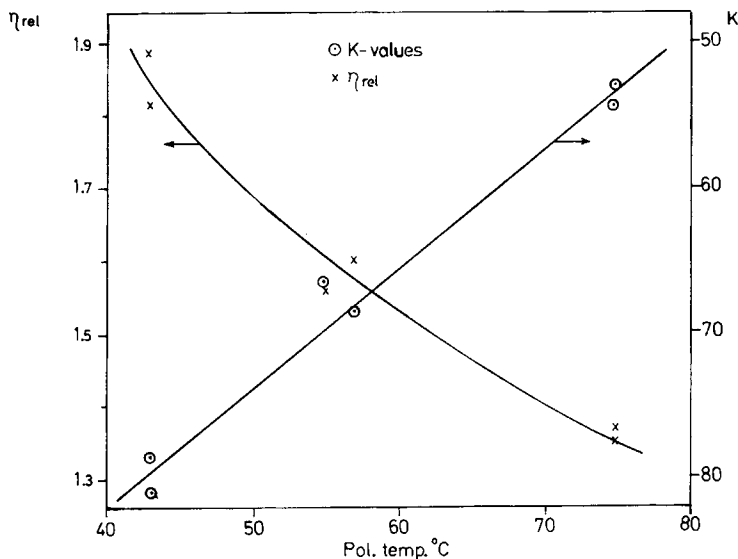


Fig. 4.  $\eta_{rel}$  and  $K$  value according to Fikentscher plotted as a function of polymerization temperature PT of PVC.

ISO Viscosity number:

$$“\eta_{red}” = \frac{\eta - \eta_0}{\eta_0 \cdot C} = (\eta_{rel} - 1) \frac{1}{C}$$

$K$  Value according to Fikentscher<sup>12</sup>:

$$\log \eta_{rel} = C \cdot \left[ \frac{75K^2}{1 + 1.5KC} + K \right]$$

where  $C$  = concentration in g/100 ml.

The ranking of these measures was not discussed seriously. In spite of its empiric and complicated relation to measured quantities, the use of  $K$  is firmly established in industry, presumably due to its linear relation to PT (Fig. 4).

The  $\eta_{rel}$  and viscosity number are not simply related to PT. In one laboratory, an Ubbelohde viscometer of about the same construction as an approved ISO viscometer was used. The uncorrected results obtained with this viscometer were in good agreement with the rest of the measurements. According to Andersson,<sup>13</sup> a correction for kinetic energy loss was calculated from the dimensions of the viscometer. When this correction was applied, slightly higher viscosity values were obtained, well outside the scatter of the rest of the measurements. It may be concluded that correction terms should not be calculated but estimated experimentally. It may be further concluded that no special correction is necessary if the ISO or DIN standards are applied. For proper characterization work,  $[\eta]$  must be used (see concluding paragraph).

In Figure 5,  $[\eta]_{THF}^{25^\circ C}$  is related to  $(\bar{M}_w)_{LS}$  in a log-log diagram in order to illustrate the correlation between the viscometric and LS measurements performed. Although the data points are very few, a Mark-Houwink equation was calculated via a linear regression analysis. The result is compared with the most widely accepted Mark-Houwink relation for PVC.<sup>14</sup> The deviation between



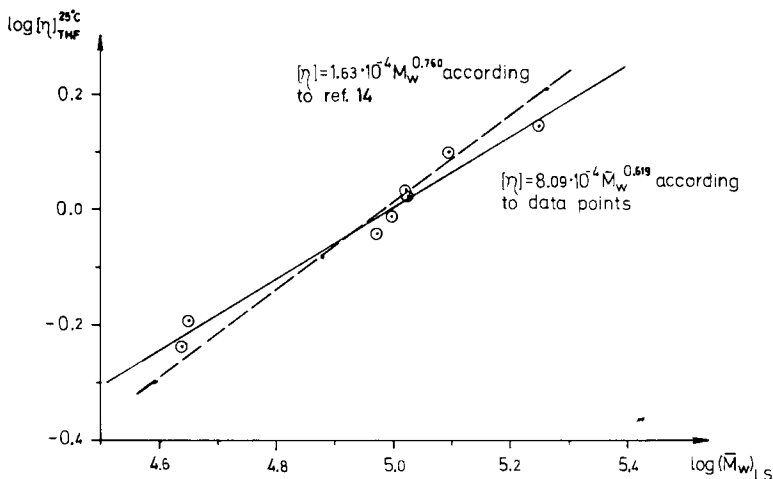


Fig. 5. Relation between  $[\eta]_{\text{THF}}^{25^\circ\text{C}}$  and  $(\bar{M}_w)_{\text{LS}}$ .

this function and the data points in the middle of the diagram is small, while the few points at both extremes show a considerable deviation, presumably due to the LS measurements (cf. Fig. 2). As to the high accuracy of the  $[\eta]$  measurements, this is illustrated in Figure 1.

### Measurements of Tacticity

Determination of tacticity was performed by infrared, Raman, and NMR spectroscopy. In connection with this work, a special investigation was carried out at the University of Helsinki. In the report,<sup>15</sup> a thorough discussion of the experimental technique is given. As the steric structure of PVC has only little influence on the position of the absorption bands, tacticity determinations are hampered by extensive overlapping of spectral peaks. This may result in wrong assignments in the relation between structure and band position. It also calls for intricate curve resolution methods in quantitative determinations. NMR spectroscopy is by far the most accurate method for measurements of tacticity. Using this technique, both qualitative and quantitative investigations were carried out.

NMR spectra were determined with Varian 60 and 100 Mc instruments on *o*-dichlorobenzene solutions at 140°C. A qualitative comparison between the spectra obtained from both instruments shows that the variation in the degree of syndiotacticity is very small among polymers E-54, E-67, E-80, S-54, R-24, and S-80. No exact correlation to the PT can be deduced from the present data owing to the narrow range of temperatures. However, it is well known that the syndiotacticity increases with decreasing Pt.<sup>16</sup>

In the quantitative determinations, the NMR spectrum of the methylene groups of polymer S-80 was resolved graphically into six bands, which were assigned to syndiotactic, isotactic, and combined sequences. By comparing the areas of the syndiotactic bands to the area of the total band complex, a measure,  $\alpha$ , of the amount of syndiotactic dyades was obtained. A computer-based curve resolving technique was also tested on polymer R-24. For polymer S-80,  $\alpha$  was found to be 0.56. Accordingly, slightly more than half of the dyades were syn-

TABLE XIV  
 Tacticity Measurements

PVC resin	IR	Raman	NMR
	$A_{1428}/A_{1435}^a$	$A_{1428}/A_{1435}^a$	$\alpha^b$
S-54	1.05	1.17	0.52
	1.10		
Pevikon R-24	1.10	1.20	0.54
	1.17		
S-80	1.15	1.23	0.56
	1.21		
E-54	1.04	—	0.51
	1.09		
E-67	1.12	1.21	0.55
	1.16		
E-80	1.15	—	0.56
	1.22		

<sup>a</sup> Tacticity evaluations using absorbance ratio  $1428\text{ cm}^{-1}/1435\text{ cm}^{-1}$  in IR and Raman spectroscopy according to H. Germar, K.-H. Hellwege, and U. Johnsen, *Makromol. Chem.*, **60**, 106 (1963), and P. J. Hendra, *Adv. Polym. Sci.*, **6**, 151 (1969).

<sup>b</sup> Amount of syndiotactic dyades, see text.

diotactic. Using this value as a standard, a simplified, relative calculation method was used for the other polymers. As expected, the syndiotacticity is decreasing with PT, but the tendency is quite weak (Table XIV).

Infrared spectra were determined on films cast from THF solutions using Beckman IR-9 and Perkin-Elmer 457 grating spectrometers. The ratio between the absorbances at  $1428$  and  $1437\text{ cm}^{-1}$  was taken as a rough measure of syndiotacticity.<sup>17,18</sup> A slight tendency toward an increase in syndiotacticity was found with decreasing PT (see Table XIV). Other absorbance ratios were also tested with about the same result.

Raman spectra were determined on PVC powders with a Spectra Physics Model 147 Kr  $\pm$  laser at  $6471.0\text{ \AA}$ ,  $100\text{--}200\text{ mW}$ , coupled to a Jarrel-Ash 25-107 double-slit monochromator with digital output. The obtained absorbance ratios at  $1428/1436\text{ cm}^{-1}$  are given in Table XIV. They show the same tendency as the infrared measurements. Other absorbance ratios were also tested.

## CONCLUSIONS

Table XV gives a summary of the experimental work, i.e., of the PVC resins used, the characterization methods tested, and the data obtained. By this study, a unique set of well-characterized PVC samples was made available for further work. The samples constitute a series of emulsion- and suspension-polymerized PVC resins within a broad range of molecular weights representative of commercial PVC qualities. For many of the resins the polymerization procedure is known.

For most characterization methods tested, remarkably good agreement between participating laboratories was reached. This applies even to such intricate methods as light scattering, LS, and osmometric determinations. A good correlation was also found between the results obtained with these methods and with gel permeation chromatography. As GPC has higher precision and accu-

TABLE XV  
Summary of Sample Characterization Data Obtained

Group	Sample	PT, °C <sup>a</sup>	$\eta_{rel}$	$K^b$	$[\eta]_{THF}^{25^\circ C}$ , dl/g	$\bar{M}_n \times 10^{-3}$		$\bar{M}_w \times 10^{-3}$		$\bar{M}_w/\bar{M}_n$		$\alpha^c$
						Osm.	GPC	LS	GPC	LS/Osm.	GPC	
1	Corvic D65/8	—	—	—	1.05	51.5	49.7	106.0	110.8	2.06	2.23	—
	X-AB	—	—	—	1.08	53.6	48.8	105.3	112.5	1.96	2.31	—
2	S-54	75	1.35	53.6	0.58	28.3	26.2	43.6	52.7	1.54	2.01	0.52
	Pevikon R-24	55	1.56	66.9	0.91 <sup>d</sup>	43.3	43.6	93.8	90.6	2.17	2.08	0.54
	S-80	43	1.82	78.9	1.26 <sup>d</sup>	71.1	58.1	124.5	141.0	1.75	2.44	0.56
	E-54	75	1.36	54.3	0.64	30.3	27.8	44.5	58.0	1.47	2.09	0.51
3	E-67	57	1.59	68.5	1.06	47.7	42.9	99.0	100.9	2.08	2.35	0.55
	E-80	43	1.88	81.3	1.39	68.0	62.9	177.8	162.3	2.61	2.58	0.56
	Pevikon S-685	—	1.60	69.0	1.00	47.3	44.2	—	96.0	—	2.17	—
	Norvinyl S9-70	—	1.61	69.5	1.00	47.1	45.7	—	98.4	—	2.15	—

<sup>a</sup> Polymerization temperature.

<sup>b</sup>  $K$  value calculated from  $\eta_{rel}$  according to Fikentscher;  $\eta_{rel}$  determined in CH at 25°C, concn. 0.5 g/100 ml.

<sup>c</sup> Amount of syndiotactic dyades determined by NMR.

<sup>d</sup>  $[\eta]_{CH}^{25^\circ C}$ .

racy, gives much more information (molecular weight distribution and long-chain branching), and is far more versatile to use, there seems to be no advantage in using LS and osmometry if GPC is available. Knowledge of MWD and LCB is of great importance not only in scientific work but also in many industrial applications, i.e., in degradation studies, when developing new resins and in the analysis of unknown samples.

However, at present, few Nordic industries use any of the above-mentioned methods when characterizing PVC resins. Instead, they rely on simple viscometric methods, which give no information about MWD or LCB. They are thus insufficient for the above-mentioned type of work. In routine production control, however, solution viscometry according to the ISO or DIN standard procedure is quite adequate, being accurate, fast, versatile, and inexpensive. According to information from KemaNord AB,<sup>19</sup> a standard deviation of 0.01 in relative viscosity is to be expected in normal production control.

Reporting the results as Fikentscher *K* values has no physical sense, but is a concession to conservative commercial usage. The viscosity number or the relative viscosity is a more direct and proper measure. Use of the intrinsic viscosity  $[\eta]$  for routine production control is much more time consuming and is not necessary when the samples are quite similar in structure. However, when elucidating the molecular weight and structure of unknown samples,  $[\eta]$  must be used as only this viscometric measure is related to structure peculiarities such as LCB and segments of abnormal mobility.

Because tacticity in PVC is restricted to very short chain sequences, only spectroscopic methods are available for such determinations. These methods are, however, hampered by extensive overlapping of spectral peaks. This calls for intricate curve resolution methods. NMR spectroscopy is much more accurate for quantitative tacticity determinations than infrared or Raman spectroscopy. According to the present measurements, PVC resins of ordinary commercial type show only small differences in tacticity. When working with such polymers, there is obviously little need for tacticity determinations.

## Appendix I

### Polymerization Procedure for S-54 and S-80

Extract from letter in Swedish written by Dr. Sten Porrvik, KemaNord AB 1971-08-13:

The polymerizations were carried out in 14-liter stainless steel autoclaves. Six runs were made at 43°C and ten at 75°C. The polymers obtained at each temperature (24 kg) were separately homogenized.

S-54	Parts by weight
6.9 kg Distilled water	135
5.1 kg Vinyl chloride	100
5 g Hydroxypropylmethylcellulose	0.098
1 g Azobisisobutyronitrile	0.020
Agitation	475 rpm
Temperature	75°C
Time	9 hr (average)
Pressure	15.5 kg/cm <sup>2</sup>
Polymerization stopped at	6.0 kg/cm <sup>2</sup>
Particle size	100–400 $\mu$ m

Charge filtered off and washed. Dried at 50°C. Moisture content 0.03%.

S-80	Parts by weight
6.5 kg Distilled water	128
5.1 kg Vinyl chloride	100
1.9 g Hydroxypropylmethylcellulose	0.037
8.5 g Dicetyl peroxydicarbonate	0.17
Agitation	475 rpm
Temperature	43°C
Time	8 h (average)
Pressure	7.3 kg/cm <sup>2</sup>
Polymerization stopped at	4.5 kg/cm <sup>2</sup>
Conversion	90 %
Particle size	100-400 μm
Charge filtered off and washed. Dried at 50°C. Moisture content 0.03%.	
Impurities in Vinyl Chloride:	
Butadiene	~10 ppm
1-Chloromethane	~50 ppm
Acetylenes	<1 ppm
1,2-Dichloroethane	~1 ppm
Impurity content of the polymer equals added suspensionstabilizer and initiator, i.e., S-54, 0.1%; S-80, 0.2%.	

## Appendix II

### Polymerization Procedure for E-54, E-67, and E-80

Extract from letter in Norwegian written by Dr. Odd Palmgren, Norsk Hydro A/S 1971-07-14:  
The polymerizations were carried out in a pilot plant reactor. Two runs were made at each temperature. The latices from the same temperature level were mixed and spray dried at 60°C.

Polymer	Polymerization temperature, °C	Initiator content, % of monomer
E-54	75	0.011
E-67	57	0.033
E-80	43	0.270
Conversion		~89%
Size of primary particles		~0.3 μm
Size of particles formed during spray drying		5-30 μm
pH		3-4
Moisture content		0.15-0.20%
Impurities in Vinyl Chloride:		
Butadiene		~10 ppm
1-Chloromethane		~200 ppm
Content of aid chemicals		~1.5%
Emulsifier:	dialkyl sulfosuccinate, alkyl sulfate	
Buffer:	phosphate	
Initiator:	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	
Initiator and buffer added before heating.		

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