

Molecular Aggregation in Poly(vinyl Chloride)

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Synopsis

PVC synthesized in a bulk polymerization at -25°C was fractionated by preparative GPC. The eluent THF solutions consist largely of dissociated molecules. Following precipitation into methanol, recovered PVC fractions contain aggregated molecules and are partially insoluble in THF. The soluble portions produce distorted chromatograms characteristic of molecular aggregation. The aggregate fraction increases with molecular weight. Heating recovered PVC fractions at 90°C in THF was adequate to dissociate the aggregates. Following recovery, fractions of PVC do not show crystalline x-ray diffraction patterns. The PVC fractions were crystallizable by subsequent annealing at 150°C to approximately 15% crystallinity, largely independent of molecular weight.

INTRODUCTION

The assumption that polymer molecules behave independently in dilute solution is often implicit in the molecular characterization of polymers from the properties of dilute solutions. This supposition is invalid when concentration independent molecular aggregation persists in solution. Molecular weight and size information derived from poly(vinyl chloride) (PVC) solutions is often distorted because the polymer is not molecularly dispersed.¹ The association of PVC molecules into densely packed aggregates in dilute dioxane solution was demonstrated by a variety of experimental techniques.² Molecular clusters of PVC have been dispersed by heating dilute solutions^{2,3} or by ultrasonic treatment.⁴

The formation of molecular aggregates in solution may be viewed as incipient crystallization and should be related to molecular perfection. With decreasing temperature of polymerization, PVC molecules are increasing syndiotactic^{5,6} and tend to form aggregates.⁷ The distortion of gel permeation chromatograms (GPC) provides a measure of aggregate formation which may be the most sensitive determination of tacticity.⁷ The aggregate component in PVC prepared at 40°C was isolated by preparative GPC and characterized following heating.⁸ The molecular weight distribution in the aggregate was similar to that of the original polymer. This would imply that aggregate formation is independent of molecular weight. Since aggregation probably involves the association of stereoregular segments, the weight fraction of clusters might be expected to be a function of molecular weight. Thus, if one large molecule is tied

in at a single point, the entire molecule is included in the aggregate. Accordingly, molecular size fractions of PVC were isolated by preparative GPC and examined for aggregate formation in dilute solution.

EXPERIMENTAL DETAILS AND RESULTS

Preparation of Poly(vinyl Chloride)⁹

Vinyl chloride monomer (600 g) was condensed at -25°C and polymerized isothermally with tri-*n*-butylboron (1 g) and azobisisobutyronitrile (1 g) initiators. Polymerization was terminated by the addition of hydroquinone, the residual vinyl chloride monomer was evaporated, and PVC polymer recovered by filtration following the addition of methanol. The resultant yield of PVC approximated 20 g ($\sim 3\%$ conversion).

Characterization

A solution of the whole polymer in tetrahydrofuran (THF) was prepared at a concentration of $\frac{1}{8}\%$ (w/v), filtered through silver "metal membrane" filters ($0.45\ \mu$, Sela Flotronics), and injected into GPC (Waters Associates, Anaprep). GPC was conducted in THF carrier solvent at 25°C by using a series of four 4-ft polystyrene gel (Styragel) columns, of 10^6 , 10^5 , 10^4 , and $10^3\ \text{\AA}$ porosity (Waters Associates) and a differential refractometer detector. The solvent flow rate was 1.0 ml/min. The experimental chromatogram is shown in Figure 1.

Calibration was effected¹⁰ by measuring the elution volumes and intrinsic viscosities of monodisperse polystyrene samples (Pressure Chemical Co.) and constructing a universal calibration curve (i.e., a plot of the logarithm of the product of intrinsic viscosity and molecular weight versus elution volume¹¹).

Commercial bulk PVC (Hooker Chemical Co., Ruco Division) was fractionated by preparative GPC and characterized by GPC elution volume and intrinsic viscosity. These data were combined with the universal

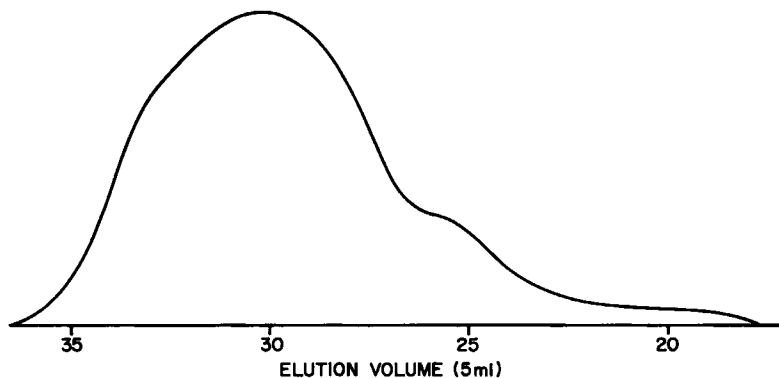


Fig. 1. Gel permeation chromatogram (GPC) of poly(vinyl chloride)(PVC) synthesized at -25°C .

calibration curve in order to generate a calibration curve specific for PVC of this type. Alternatively, a calibration relating PVC and polystyrene via intrinsic viscosity-molecular weight relations gave similar results.¹² The number- and weight-average molecular weight corresponding to Figure 1 are 9,700 and 458,000, respectively.

Fractionation

Chromatographic fractionation of PVC synthesized at -25°C was effected by preparative GPC (Anaprep, Waters Associates) using three preparative columns (4 ft \times 2.5 in.) packed with Styragel having a range of porosities from 5×10^3 to 1.5×10^5 Å. A 0.5% solution of PVC was prepared by refluxing in tetrahydrofuran (THF) at 65°C and aliquots of the solution injected continuously and automatically over a period of 28 hr. Solvent flow rate was adjusted to 50 ml/min with the collection of effluent programmed at 180-ml increments; 21 fractions contained in 2.5-liter solutions were collected. Portions, 50 ml, of each solution were concentrated tenfold by evaporation in a stream of nitrogen and injected into analytical GPC yielding chromatograms of unrecovered fractions. The same analytical GPC technique was used for fractions and whole polymer. Resultant peaks were interpreted as described above. Gel permeation chromatograms of some of the fractions are superposed on the chromatogram of the whole polymer in Figure 2 and are designated as chromatogram A in Figures 3 to 7. Basic characterization data derived from GPC on unrecovered polymer solutions are tabulated in Table I. The numbering of fractions is arbitrary and refers to ordered containers; W is the final recovered weight of each fraction, \bar{M}_w and \bar{M}_n , the corresponding weight-

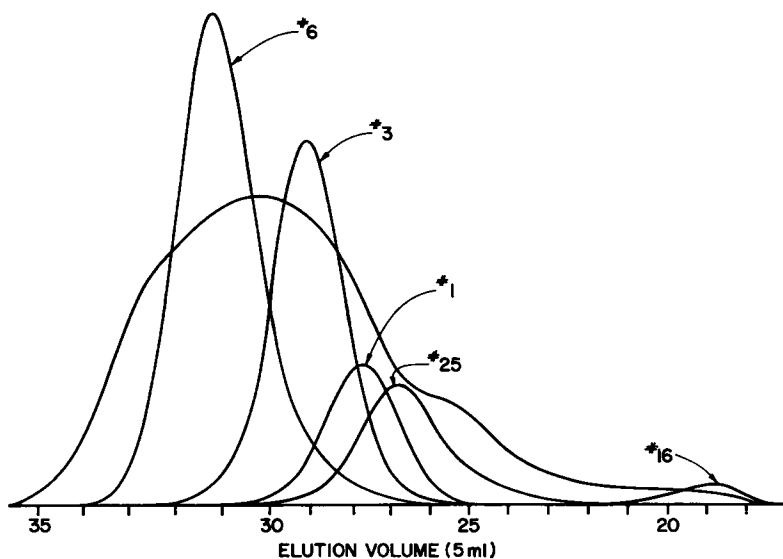


Fig. 2. Chromatograms of eluent aliquots from preparative GPC superposed on Fig. 1.

TABLE I
 Fractionation of Low-Temperature Poly(vinyl Chloride)

Fraction no.	W, g	\bar{M}_w	\bar{M}_w/\bar{M}_n	Aggregate fraction, %
16	.0412	14,100,000	1.04	
17	.0381	12,600,000	1.72	
18	.0315	8,150,000	3.27	
20	.0691	1,530,000	2.35	
21	.1060	839,000	1.92	
22	.1462	456,000	2.04	
23	.1009	724,000	2.37	
24	.1153	300,000	1.61	
25	.1165	216,000	1.61	37.7
0	.1556	145,000	1.43	
1	.2153	94,200	1.23	28.2
2	.2830	68,000	1.25	
3	.2973	48,700	1.26	7.7
4	.3598	36,400	1.27	
5	.3681	27,800	1.25	
6	.4022	18,100	1.32	2.0
7	.3982	12,000	1.37	
8	.3982	7,600	1.50	
9	.2619	5,400	1.59	
10	.1386	4,400	1.81	
11	.0498	3,900	2.16	

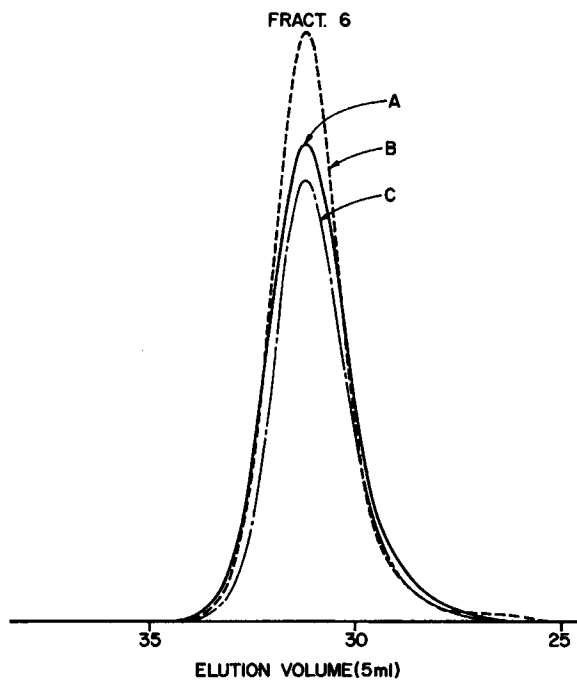


Fig. 3. Fraction 6, $\bar{M}_w = 18,100$: (—) A, GPC effluent; (---) B, THF-soluble portion after precipitation; (-·-·-) C, THF-soluble portion after heating in THF at 90°C.

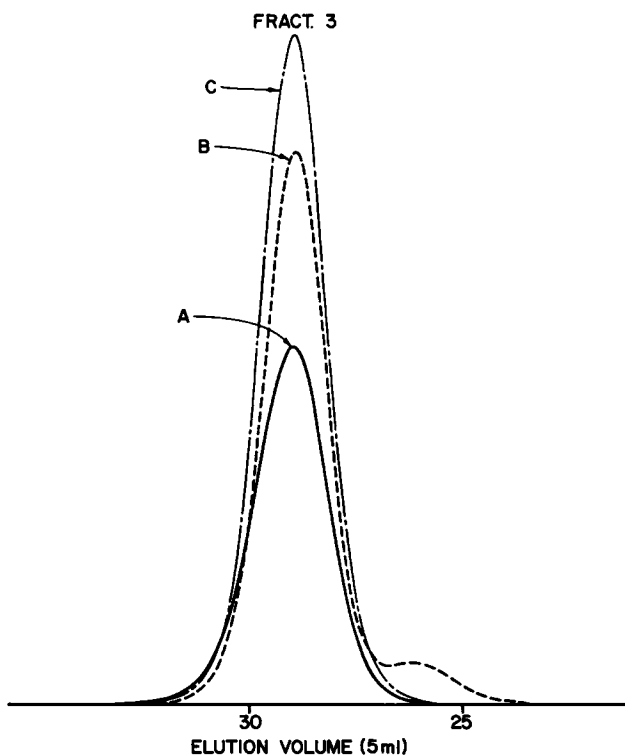


Fig. 4. Fraction 3, $\bar{M}_w = 48,700$: (—) A, GPC effluent; (---) B, THF-soluble portion after precipitation; (- - - -) C, THF-soluble portion after heating in THF at 90°C.

and number-average molecular weights, respectively, and \bar{M}_w/\bar{M}_n , their ratio. The final column records the fractional area of the chromatogram of recovered fractions attributed to aggregation (cf. curve B, Figs. 3-6).

The dilute polymer solutions resulting from preparative fractionation were concentrated approximately tenfold by distilling off THF and by an additional factor of 7 by evaporation in a stream of nitrogen. About 30 ml of each of the resulting concentrated solutions was added slowly with stirring to 300 ml absolute methanol at 25°C. Precipitates were allowed to settle, excess supernatant liquid decanted, and the remaining suspensions filtered by suction into a tared Gooch crucible (through Whatman #42 filter paper). The recovered polymer was repeatedly washed with methanol and dried in a vacuum oven at 45°C and 0.5 mm for 16 hr to constant weight. Fractions of PVC after recovery from methanol were partly insoluble in THF, even on prolonged refluxing, precluding dissolution at adequate concentration for intrinsic viscosity measurements.

Solutions of the soluble portions of fractions recovered from methanol were prepared at room temperature in THF and injected into GPC. The corresponding chromatographic traces are designated B in Figure 3 to 6. Fraction 6 was fully soluble in THF at a concentration of 0.125% and

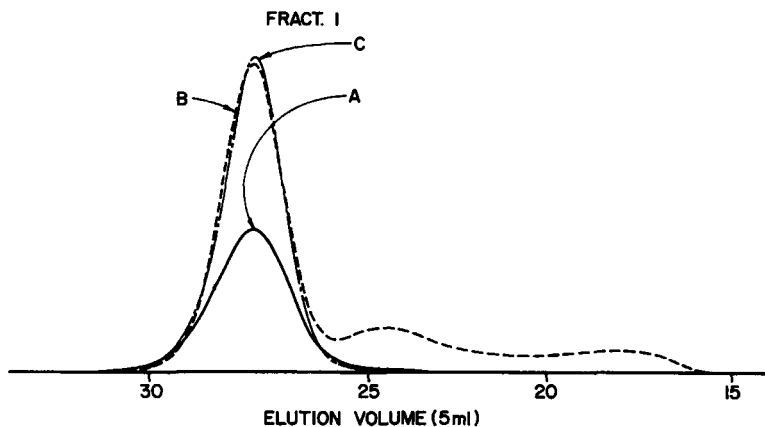


Fig. 5. Fraction 1, $\bar{M}_w = 94,200$: (—) A, GPC effluent; (---) B, THF soluble portion after precipitation; (-·-·-) C, THF soluble portion after heating in THF at 90°C.

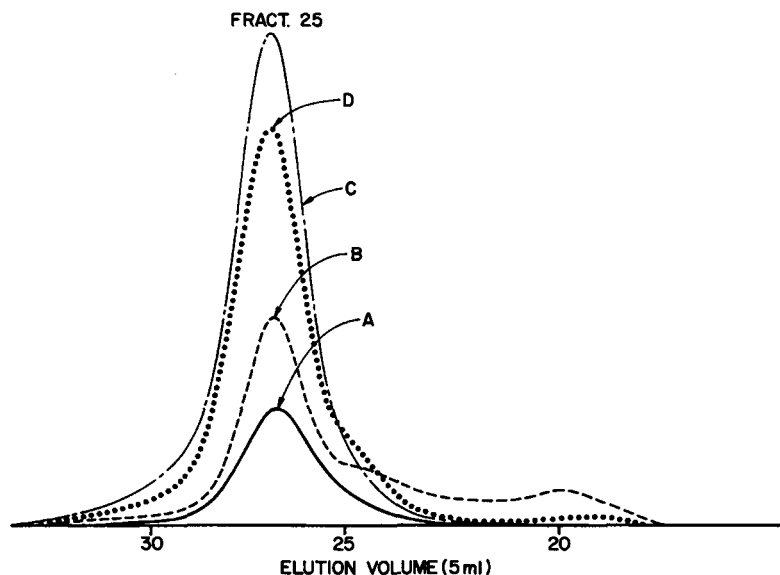


Fig. 6. Fraction 25, $\bar{M}_w = 216,000$: (—) A, GPC effluent; (---) B, THF-soluble portion after precipitation; (-·-·-) C, THF-soluble portion after heating in THF at 90°C; (.....) D, after storage of solution for 1 week.

completely chromatographed. For fractions 3, 1, and 25, gel was observed and GPC traces designated B correspond to moieties soluble in THF. Following recovery, fraction 16 was largely insoluble and not injected into GPC.

Solutions of PVC fractions in THF were prepared by weighing dried fractions into combustion tubes (Fisher-Porter), adding THF and sealing with a Teflon gasket and aluminum cap. Tubes were heated at 90°C

TABLE II
Disaggregation of PVC Fractions

Fraction no.	Time at 90°C	Figure	Comments
6	10 Minutes	3	fully soluble
3	60	4	slight gel
1	60	5	slight gel
25	90	6	slight gel
16	1,320	7	more gel

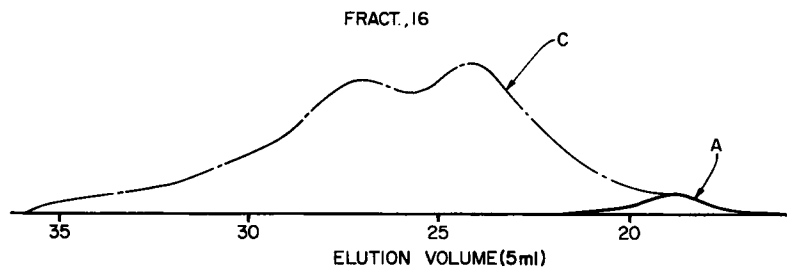


Fig. 7. Fraction 16, $\bar{M}_w = 14 \times 10^6$: (—) A, GPC effluent; (---) C, THF-soluble portion after heating in THF at 90°C.

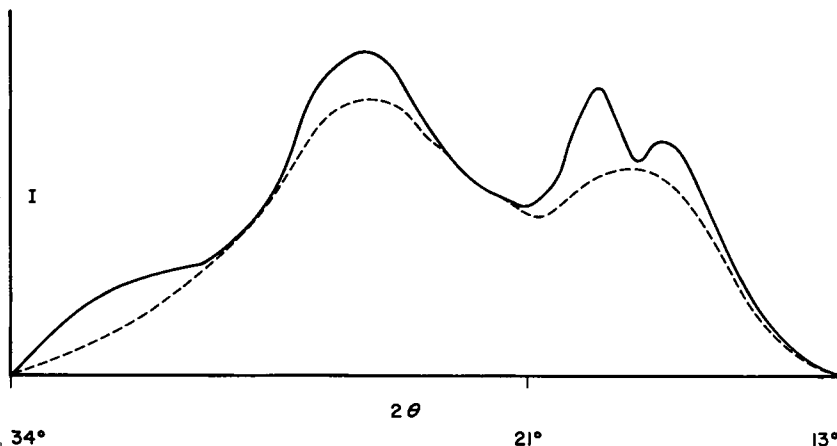


Fig. 8. X-Ray diffraction scan of fraction 4: (---) following isolation; (—) after annealing at 150°C for 30 min.

for various time periods and soluble portions injected into GPC. Specific treatments are summarized in Table II, and resultant traces are designated curve C in Figures 3 to 7.

Although GPC data are reported for only five fractions, additional GPC data were measured and are completely consistent. All the solutions were colorless following treatment with THF at 90°C, suggesting that degradation did not occur.

There is some evidence of reaggregation following storage at 25°C of a PVC fraction previously disaggregated by heating at 90°C. Fraction 25

was stored for one week at 25°C following 90 min of heating at 90°C. A high molecular weight tail (curve D, Fig. 6) is evident.

X-Ray diffraction scans of PVC samples were generated between 2θ values of 13° and 34° using an x-ray diffractometer (Phillips Norelco) with a copper-target x-ray tube ($\lambda = 1.54 \text{ \AA}$). X-Ray diffraction from fraction 4 before and after annealing is illustrated in Figure 8. X-Ray diffraction crystallinity was approximated by the fractional area of crystalline diffraction peaks.¹³ Samples were examined at 25°C following isolation and after annealing at 150°C for 30 min. Data are summarized in Table III.

TABLE III
X-Ray Diffraction Crystallinity of PVC Fractions

Fraction no.	As recovered, %	Annealed, %
24	0	15
4	0	14
8	0	19

DISCUSSION

The molecular weight data recorded in Table I for PVC fractions were calculated from GPC without consideration of extraneous broadening. A comparison with monodisperse polystyrene standards indicates that the correction to the ratio \bar{M}_w/\bar{M}_n approximates 20% for these columns. Thus, ratios of \bar{M}_w/\bar{M}_n of 1.25 indicate true polydispersities of about 1.05.

GPC molecular weights of the highest molecular weight fractions in Table I are meaningless. These materials elute near the interstitial volume or exclusion limit of the gel columns where resolution is highly imperfect. Moreover, these observed elution volumes were in an uncalibrated region of GPC. The apparent narrowness of the two highest molecular weight fractions is an artifact associated with poor resolution and with aggregation as shown in fraction 16 (Fig. 7).

The PVC synthesized at -25°C has an unusually broad molecular weight distribution (Fig. 1). The asymmetry and high molecular weight tail might be ascribed to molecular aggregation in THF solution. However, solutions of unrecovered fractions resulting from preparative GPC fractionation of this material produce unimodal GPC peaks which are identical to those produced by recovered fractions following dissolution by heating at 90°C (compare curves A and C in Figs. 3-6). Moreover, another PVC whole polymer synthesized according to the procedure described at -20°C was analyzed by GPC following complete dissolution by prolonged refluxing in THF. The resultant chromatogram was very similar to that illustrated in Figure 1. GPC was then conducted on this

material following heating in THF for 90 min at 90°C. The chromatogram was largely unaffected by this treatment. It is concluded that the PVC solution is *largely* disaggregated following dissolution of the whole polymer at very low concentrations. As a result, the solutions eluting from preparative GPC contain separated PVC molecules. Chromatograms corresponding to successive eluent solutions are shown as curves A in Figures 3-7. The chromatogram of unrecovered fraction 16, the very highest molecular weight fraction, was the only one altered by heating the corresponding recovered fraction at 90°C in THF (Fig. 7), indicating extensive aggregation of this component. This observation will be discussed subsequently.

Following precipitation into methanol, all the fractions were partly insoluble in refluxing THF at concentrations approximating 1%. The isolated PVC fractions apparently contained highly aggregated molecules as supported by the bimodal GPC of soluble portions. Association was assumed to occur on the precipitation and isolation of the fractions. This insolubility is in marked contrast to PVC synthesized at 50°C, in which recovered fractions were readily soluble in THF and showed unimodal distributions. These solubility and chromatographic differences probably result from variations in chain regularity. PVC synthesized at -25°C and isolated at low conversion has a more linear, head-to-tail, syndiotactic structure than PVC synthesized at 50°C. Following preparative GPC separation and recovery, these PVC molecules, which are now regularized as to molecular weight as well, aggregate sufficiently to preclude complete dissolution in THF, even at its boiling point.³

The fractions selected for study include a wide range of molecular weights (Fig. 2). The curves corresponding to the individual fractions are effectively normalized to the weight fraction of each component by the injection of a fixed volume of GPC effluent.

Soluble portions of recovered fractions prepared at room temperature or by refluxing in THF at a concentration of 0.125% produced chromatograms containing a high molecular weight tail (curve B in Fig. 3). Moreover, fractions 3, 1, and 25 (curves B in Figs. 4, 5, and 6) produced multimodal chromatograms suggesting that discrete distributions may be distinguishable. To the extent that a calibration and elution volumes based on linear polymer can be applied to GPC of aggregated molecules, the molecular weights for successive peaks in the multimodal chromatograms was estimated. The molecular weight of the first "aggregate peak" in Figures 4, 5, and 6 approximates six times that of the corresponding disaggregated species. The aggregate apparently consists of many molecules. The proportion of the high molecular weight tail increases with molecular weight (Table I). Thus, fraction 6, which is fully soluble at a concentration of 0.125%, and the soluble portions of fractions 3, 1, and 25 have increasing amounts of a high molecular weight tail which is associated with molecular aggregation. Insolubility of the highest molecular weight fraction (16) in THF is interpreted as resulting from extensive molecular aggregation.

Fractions 6, 3, 1, and 25 lose their high molecular weight components (curves C in Figs. 3-6) following heating at 90°C, for the periods of time indicated in Table II. Corresponding GPC traces are virtually coincident, except for concentration differences, to GPC traces of original GPC eluents from the preparative fractionation. Heating at 90°C apparently is adequate to disaggregate these PVC molecules.

Fraction 16 which, following recovery, is insoluble in refluxing THF, yields a soluble moiety on prolonged heating in THF at 90°C. The resulting chromatogram has a bimodal character and is very broadly distributed compared to that resulting from the original solution (Fig. 7). Apparently, a very broad range of molecular weights is included in this fraction. Heating at 90°C for prolonged periods is inadequate to disaggregate even the soluble portion of fraction 16 fully. Apparently, the unrecovered fraction 16 in the preparative GPC eluent is highly associated (curve A, Fig. 7). The most perfect molecular configurations, regardless of molecular weight, may be segregated in this fraction. The occurrence of branching in the highest molecular weight fractions of PVC was suggested to account for deviations from linearity in the double logarithmic plot of weight-average molecular weight and intrinsic viscosity.¹⁴

The evidence for reaggregation following storage at 25°C as illustrated in Figure 6 is meager, but suggestive. The formation of associated PVC molecules following dissociation by heating will be the subject of further studies.¹

Although the solid fractions of PVC were highly associated following precipitation from solution, crystallinity was *not* detected by x-ray diffraction (Table III). Although aggregation and crystallinity are related to molecular perfection, they are not identical parameters. Crystallinity detected by x-ray diffraction requires a three-dimensional ordering of syndiotactic segments.¹⁵ Aggregation may correspond to a two-dimensional mesophase and is probably the origin of the bimodal structure in the amorphous halo in x-ray scattering from these materials.¹⁶ It must be pointed out that PVC synthesized at temperatures in excess of 50°C exhibit similar x-ray patterns but do not evidence aggregation in dilute solution.

Although dried fractions were not crystalline, they are *crystallizable*. Following annealing for 1/2 hr at 150°C, a level of crystallinity approximating 15% is observed in all fractions investigated (Table III). To a fairly good approximation, ultimate crystallinity is independent of molecular weight. Crystallinity is not suppressed in molecular weight fractions of PVC, at least up to fraction 24, $\bar{M}_w = 300,000$. This observation indicates that the level of molecular perfection (presumably tacticity) depends only on polymerization temperature⁵ and is independent of molecular weight.

The apparent dependence of aggregation on molecular weight (Table I) is amplified by the measurement we are making. For x-ray diffraction crystallinity, we measure the fraction of material that is crystalline. In

the aggregation studies, we record changes in molecular size resulting from aggregation. At a constant fraction of monomer units that are involved in aggregates, the fraction of aggregated polymer molecules increases with increasing chain length.

CONCLUSIONS

PVC synthesized in a bulk polymerization at -25°C had an unusually broad molecular weight distribution which, following dissolution in THF and GPC separation, consists largely of dissociated molecules. Following the precipitation of eluent solutions from preparative GPC into methanol, PVC fractions contain aggregated molecules and are partially insoluble in THF. The soluble portions produce distorted chromatograms characteristic of molecular aggregation. The aggregate fraction increases with molecular weight and apparently consists of many molecules.

Heating recovered polymer fractions in sealed tubes at 90°C in THF for various periods of time, increasing with molecular weight, yielded in most cases chromatograms identical to those from original solutions eluting in preparative GPC. Such treatment was adequate to dissociate the supermolecular aggregates of PVC. The very highest molecular weight fraction was shown to be highly aggregated during preparative GPC and to dissociate on heating at 90°C to a broad range of molecular weights. This fraction is probably composed of the most perfect molecular configurations.

Solid fractions of PVC containing supermolecular aggregates after precipitation from solution do not evidence crystalline x-ray diffraction patterns. It is suggested that the ordering of PVC chains in aggregates is not adequately developed in three dimensions to produce crystalline diffraction. The PVC fractions were crystallizable by subsequent annealing at 150°C to approximately 15% crystallinity, largely independent of molecular weight.

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