

The Utilization of DSC in Studies of Oligomers

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Synopsis

Oligomers are potentially useful as well characterized models for studying the chemical and physical properties of their long chain homologues. These model compounds are often available only as mixtures which must be separated. This separation may be accomplished using chromatographic techniques, i.e., GPC. Polydispersity (M_w/M_n) is often used as a criteria for the extent to which separation has been achieved. Values of polydispersity of 1.01–1.03 are considered indicative of very narrow fractions in the high polymer area. A purpose of this paper is to show that such low values of polydispersity are misleading when applied to oligomers containing 2–20 repeat units. Further, the existence of a single "sharp" melting endotherm is not necessarily proof that one has separated out a single molecular weight component. An intimate mixture of different molecular weight oligomers can give a single narrow endotherm.

INTRODUCTION

A number of oligomer studies have been reported in the literature. Studies of this type are usually aimed at understanding the properties of polymeric materials by first understanding how the properties of the oligomer vary as a function of chain length. In order to accomplish this, one must obtain relatively pure samples of these oligomers, and one must also be able to characterize the number of repeat units within the oligomer. Oligomers are often available as mixtures via some particular synthetic route. This mixture is then fractionated to obtain pure components. Recently, the Dow Chemical Co. has developed a method¹ to synthesize oligomers of vinylidene chloride (VDC). These, of course, are potentially useful as a well-characterized model for studying the chemical and physical properties of poly(vinylidene chloride) and its copolymers.

Fractionation of oligomer mixtures is often carried out using a chromatographic technique. It is also possible to use the technique to identify how well the fractions have been separated. For example, in the gel permeation chromatography (GPC) area one would normally characterize the narrowness of a particular distribution in terms of polydispersity. This is defined as M_w (the weight average molecular weight) divided by M_n (the number average molecular weight). The narrowest polymer fractions have polydispersities whose values are approximately 1.01–1.02. This technique was used on the vinylidene chloride oligomer samples and produced fractions whose polydispersities were on the order of 1.02–1.03. By normal standards these values would be considered indicative of extremely narrow molecular weight distributions. In the case of oligomers, where we are dealing with numbers of repeats in the chain on the order of 2–20, such values of polydispersity are highly misleading. Samples with very low values of polydispersity can contain a much broader distribution of oligomer

sizes than is desirable for the normal studies one wishes to carry out on such materials.

The Dow Chemical Company kindly made milligram samples of VDC oligomers available to us. The samples had previously been characterized by GPC and by this technique would be considered effectively monodispersed. A preliminary study of the melting point of these oligomers, carried out at The Pennsylvania State University, convinced us that the "as-received" samples were not truly monodispersed. We, therefore, initiated an attempt to further fractionate these oligomer samples. After additional fractionation, we attempted to distinguish between the components so obtained by using differential scanning calorimetry (DSC).

EXPERIMENTAL

Fractionation of the "as-received" oligomer samples was performed using techniques similar to those already reported in the literature.² The oligomer was dissolved in methanol and selectively precipitated using water as a nonsolvent. This process was carried out over a temperature range of 40–50°C ($\pm 0.05^\circ$ at any temperature). The total initial sample weight was on the order of 50–100 mg. Water was added to the solution of oligomer in methanol until approximately half the sample had precipitated. The precipitate in the mother liquor was separated by pulling off the liquid using a water aspirator. Additional water was added to the liquid in order to precipitate more of the oligomer. The solid sample was redissolved in methanol and, again, we separated it into two components by the addition of water.

Using this scheme, and "as-received" oligomer sample was further subdivided into approximately eight different components, depending on the solubility/insolubility in a particular water/methanol mixture. After separation the solids were dried in air and finally under high vacuum; both procedures were performed at room temperature. Melting endotherms were determined using a Perkin Elmer DSC 2. Typical sample sizes were on the order of 1–2 mg.

RESULTS AND DISCUSSION

Traces of the thermograms obtained from both the "as-received" oligomer, and the components which we derived from it are shown in Figures 1 and 2. It should be noted that the "as-received" oligomer was considered to be a very narrow "fraction" with a polydispersity on the order of 1.03. However, in both cases reported we have been able to take these "fractions" and further fractionate them into components with considerably different melting points: different from each other and from the "as-received" sample. In one case, the "as-received" sample gave a very narrow melting endotherm whose maximum was approximately 350 K (Fig. 1). This sample was subdivided into a number of components. The four components shown here range in melting point from approximately 340–371 K.

The second "as-received" sample also had a very narrow endotherm, which in this case was at 360 K. This sample was also subdivided into a number of components. The melting points ranged from 367 to 372 K. In this case (Fig. 2), the components themselves clearly show evidence of multiple melting en-

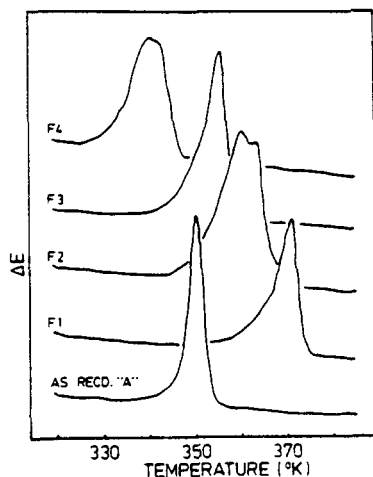


Fig. 1. "As recd. A" is a fraction with a nominal M_n of ~ 1200 and $M_w/M_n = 1.027$; F1-F4 are components obtained as described in the text.

dotherms. These multiple peaks we would associate with the melting out of different oligomers within one of our components. Presumably one could further subdivide our components with additional fractionation.

The "as-received" samples, with polydispersities of ~ 1.03 , could be subdivided into components with quite different melting points. At first this spread might appear to be surprising. However, a relatively simple and straight forward calculation can show that it should be anticipated. For example, let us assume that a sample contains oligomers with numbers of repeat units ranging from 7 to 12. If these oligomers are present in equal numbers, then one can readily calculate for this theoretical distribution an M_n and an M_w (see Table I). The polydispersity of such a sample is 1.028. By the usual standards such a polydi-

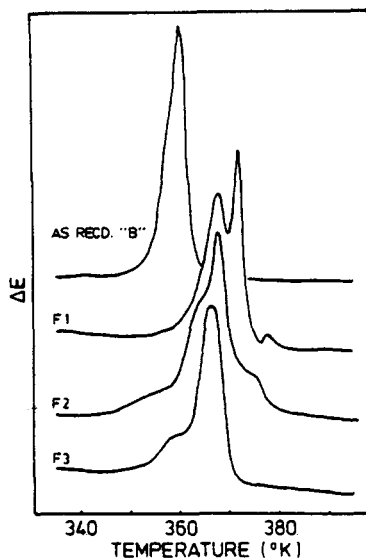


Fig. 2. "As recd. B" is a fraction with a nominal M_n of ~ 1300 and $M_w/M_n = 1.030$; F1-F3 are components obtained as described in the text.

TABLE I
 Oligomer Mol Wt Distributions

	Ni	Mi	Ni·Mi	Ni·(Mi) ²
	10	750	7,500	5,625,000
	10	847	8,470	7,174,090
	10	944	9,440	8,911,360
	10	1041	10,410	10,836,810
	10	1138	11,380	12,950,440
	10	1235	12,350	15,252,250
Total	60		59,550	60,749,950

* $M_n = 992.5$, $M_w = 1020.2$, $M_w/M_n = 1.0278$.

spersity would be considered representative of a very narrow molecular weight distribution. Clearly, for oligomer studies one must reassess the value of polydispersity indicative of a "narrow" distribution. In this particular example we are dealing with oligomers which range from 7 to 12, an approximate twofold increase in molecular weight, and yet the calculated polydispersity is indicative of a very narrow molecular weight distribution.

Although oligomers in these molecular weight ranges are not readily separated from each other using standard GPC techniques, they have sufficiently different crystallization or solubility behavior that enables them to be separated using a solution/disolution fractionation procedure. Note that paraffins with the appropriate number of carbons (14–24) differ in melting point by some 45 K. As a result, we are able to separate from an apparently narrow molecular weight distribution sample a number of components which have quite different melting behaviors. Some of these components could be further subdivided. We assume that this is the case since we are observing in the thermograms evidence of two or three separate endotherms for a particular component.

CONCLUSIONS

Clearly initial studies aimed at separating and characterizing oligomers can be very confusing. A fraction can easily give a very narrow molecular weight distribution (polydispersity). The same fraction can have a single and narrow melting endotherm and yet can be subdivided into components. The components can have higher or lower melting points; cf. the "as-received" fraction. Further, the components themselves can exhibit multiple endotherms.

This latter observation deserves some explanation. If the initial "as-received" fraction was formed by a rapid procedure (crystallization, precipitation, etc.), then presumably an intimate reasonably homogeneous mixture of the component oligomers would result. On subsequent separation, if slower, more equilibrium, procedures are followed, then phase separation of the component x-mers may occur. Such separation would give rise to the observed melting behavior, assuming individual components can contain two or more phase separated x-mers.

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