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Tracking of Alkyd-Resin Condensation by GPC

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SUMMARY

Condensation process of pentaerythritol / phtalic-anhydride/ benzoic acid/synthetic fatty acid mixture was carried out according to two different schedules; the first was carried out in one step (I) at 210 °C, the other in two steps (II) feeding pentaerythritol into the mixture of the other components already preheated to 180 °C and then elevating the temperature to 210 °C. GPC chromatograms were taken during the process. It has been established that fractions with higher molecular mass are formed from fractions with lower molecular mass. It could be proved with a three-detector method that they become chemically homogeneous starting from molecular masses of about 10 000.

INTRODUCTION

It has been already pointed out in the literature (WALZ 1977) that an alkyd resin system prepared on the basis of pentaerythritol and phtalic anhydride may grow to very large molecules, while its polydispersity remains extremely broad containing both linear and cyclic species.

Investigation of molecular masses of alkyd resins is, however, a troublesome task. The fractionation is hindered by the risk of crosslinking during this operation, light scattering measurements of weight average molecular masses are highly complicated because of the lack of suitable solvent and resin purification techniques (NAGATA 1969). In most of papers dealing with alkyd resins the measurements of molecular masses are limited to cryoscopy, both membrane and vapour osmometry and viscosity techniques, but these data fail to give information concerning polydispersity and chemical homogeneity of samples, though the latter are essential from the point of view of varnish properties.

GPC is in fact the only adequate method of full characterizing of samples in spite of its shortage that there are no appropriate fractions available for column calibration. When using the common polystyrene standard calibration-method only apparent (relative) values of average molecular masses can be obtained. It has been shown, that the deviation from the absolute molecular mass values is limited to a factor of two (WALZ 1977). If employed, GPC is a method for final product characterization (HATA et al. 1978; NAGATA 1969).

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EXPERIMENTAL

Resin preparation

A given mixture of synthetic fatty acid, phtalic acid, benzoic acid, ketone formaldehyde modifying resin, xylene and pentaerythritol was heated in a reactor to 210 °C during two hours, and then the temperature was maintained for the next 12 hours (schedule I); or a mixture of the same components except pentaerythritol was first preheated to 180 °C and after three hours pentaerythrit was introduced and temperature elevated to 210 °C and maintained for the next 11 hours (schedule II). Samples were taken in time intervals of approximately 1 hour for GPC measurements.

GPC measurements

Waters chromatograph, type ALC/GPC-201 was used with 6 columns series of pore diameter from 10^6 - 100 Å; freshly destilled THF was the eluent at ambient temperature and elution rate was 2 ml/min. 30-200 µl of 1 % resin solution was injected from each sample. Differential refractometer (RI) and UV absorption detector at two wavelengths (280 and 313 nm) were used simultaneously. The chromatograms were evaluated according to GPC calibration for polystyrene standards.

RESULTS AND DISCUSSION

The change in molecular mass distribution (MMD) in the course of reaction II evaluated according to polystyrene calibration and differential refractometer recording is illustrated in Figure 1 and 2.

During the first two hours (Figure 1) there is no change in initial composition. After the pentaerythritol had been fed (Figure 2) into the system, the common peak of benzoic acid/phthalic anhydride (log M = 2,35) suddenly diminished to one sixth of its starting value. Then during the next 11 hours only a half of the rest was consumed. Fatty acid peak (log M = 2,8) became undetectable after 7 hours of the reaction. It is plausible therefore, that the resin fractions of higher molecular masses were formed mainly from those of lower molecular masses. As polydispersity of the fractions grows, the content of lower molecular masses decreases.

The series of chromatograms registered for reaction I showed a similar qualitative picture as illustrated in Figure 2. The only difference to be seen is that components were consumed already during the first two hours of the process. The results obtained by the two different schedules are compared quantitatively in Figure 3, where the change in intensities of MMD-s for some selected maxima are presented. (The maxima have been labelled in Figure 2.) From Figure 3 it comes out that since the 10^{th} hour of the reaction the two schedules approach practically the same MMD and in the last two hours it does not change. However, we may notice (Figure 2) that in the final period a considerable fraction of the resin is shifted to the range of molecular mass over one million. This phenomenon is accompanied by limited solubility in THF.

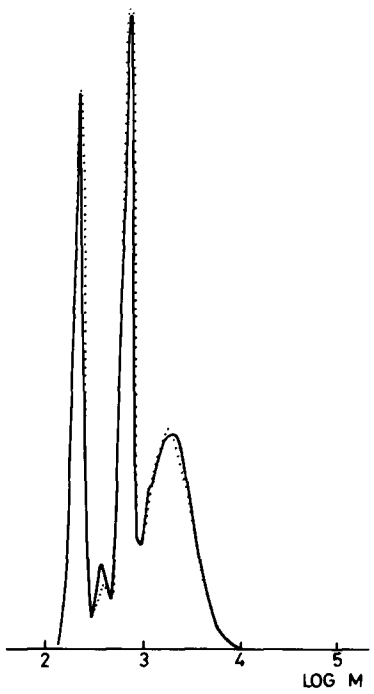

Figure 1. MMD curves for two steps schedule before feeding of pentaerythritol; — 1,5 hours reaction time; ... 2,5 hours reaction time

With help of UV detection it was possible to come to some conclusions concerning the content of these fractions with extremely high molecular masses.

The chromatograms detected by UV detector have been transformed to molecular mass scale according to the usual procedure of accounting MMD-s.

The so calculated curves for all samples have been compared with those taken with differential refractometer as for example in Figure 4. It is obvious that only the RI data give the real MMD.

UV detection on its side is strongly dependent on the structure of species. So if the curves from three different detection modes do not cover each other, there must be a discrepancy in structure of particular species.

It turns out from the comparison of RI/UV-280/UV-313 curves that for fractions of molecular mass over 10 000 the chemical composition of the resin becomes homogeneous. However, after more than 13 hours of the reaction time it becomes again heterogeneous in the range of molecular mass over one million. It is caused by a progress of crosslinking and is accompanied by solubility difficulties in THF.

The conclusions, which follow from our observations are of practical interest too: there is no considerable difference between the one step and two step schedules and the reaction cycle may be shortened. However, to avoid crosslinking the reaction time must be reduced by at least one hour.

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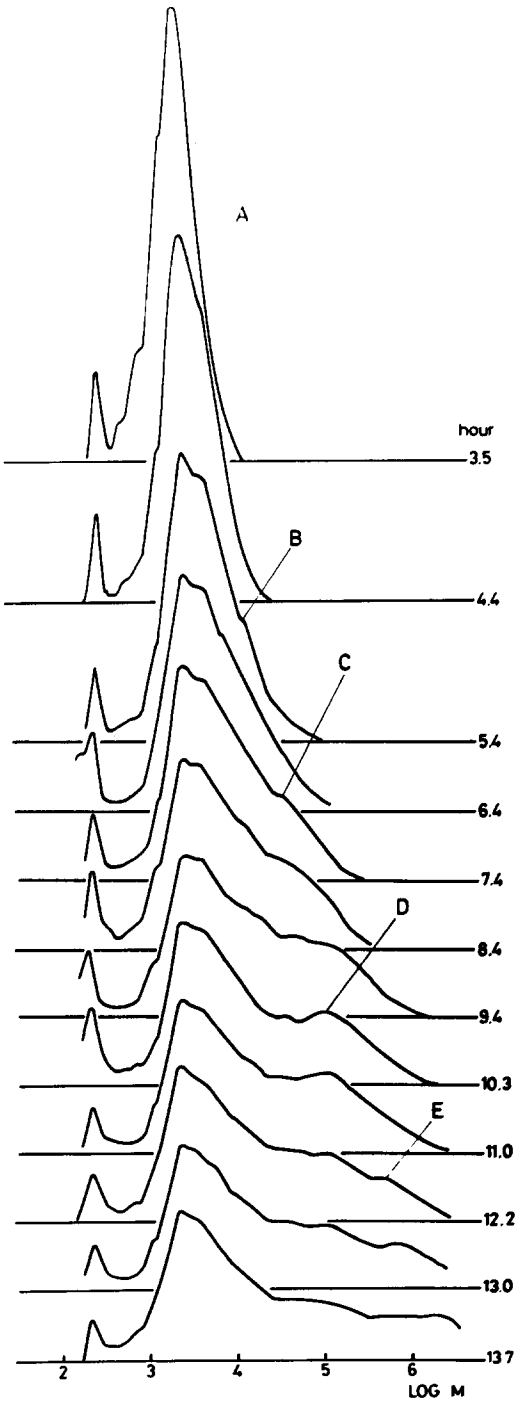

Figure 2. MMD curves for two-steps schedule after feeding of pentaerythritol. The reaction time is labelled.

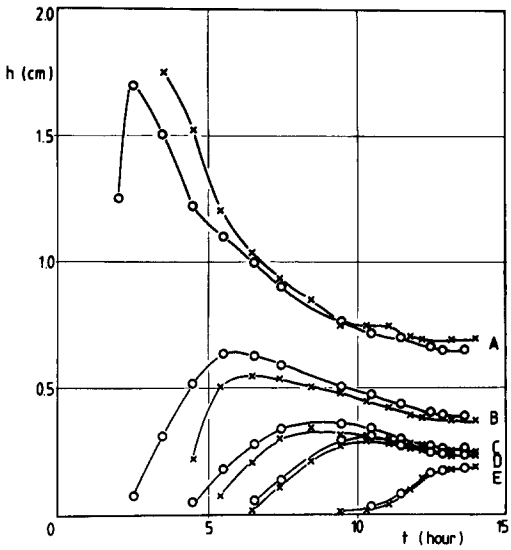

Figure 3. Change of amounts of different fractions during polycondensation:
o - one step schedule;
x - two steps schedule;
A - log M = 3.35;
B - log M = 4.00;
C - log M = 4.55;
D - log M = 5.10;
E - log M = 5.8

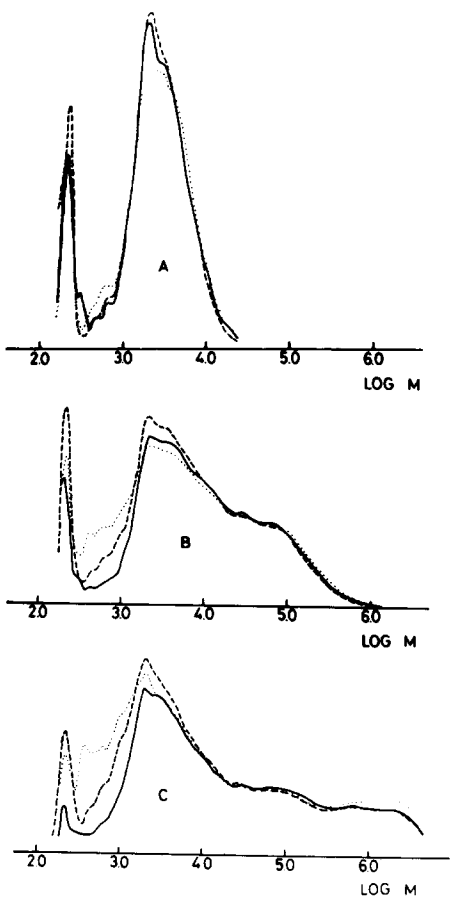

Figure 4. Comparison of chromatograms taken by three different detectors and transformed to molecular mass scale. Schedule I, Detectors:
—— RI, --- UV - 280,
... UV - 313; Reaction time:
A - t = 3.5 hours,
B - t = 9.5 hours,
C - t = 14 hours

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