Note to the Editor

Cyclic oligomers from ethylene glycol–adipic acid polycondensation

Anthony C. Davis
Research and Textile Development Department, ICI Fibres, Hookstone Road, Harrogate, North Yorkshire, UK

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The purpose of this Note is to record the formation and properties of the dimeric cyclic ester from ethylene glycol and adipic acid, 1, 4, 11, 14–tetraoxacycloeicosan–5, 10, 15, 20–tetraone (I), and present evidence that the cyclic monomer may also be formed.

In the preparation of a series of condensation copolymers of which the main structural component was ethylene adipate, the polyester component being built up from adipic acid and normally 5 to 20% molar excess of glycol, a crystalline substance was repeatedly found in the glycol distilled at the vacuum polycondensation stage. This substance was also formed when ethylene adipate homopolyester was made from adipic acid and glycol alone, and was isolated and characterized as described in the Experimental section. Its infra-red spectrum, elemental analysis, lack of functional groups, saponification value and mass spectrum identified it as the dimer (I). The expected accompanying cyclic monomer was not isolated, but its presence is inferred from gas–liquid chromatography, mass spectrum, and other analytical work on the glycol mother liquor from the dimer.

In the pioneer work of Carothers and Spanagel[1] on thermal depolymerization of linear polyesters to cyclic oligomers, three cyclic adipic oligoesters, all monomeric, were recorded, derived from C_6 to C_9 straight chain diols or oxadiols. In view of the technical importance of the two intermediates, it is surprising that ethylene adipate cyclic esters have not been recorded until now. Carothers and Spanagel found that for repeat unit lengths of 8, 9, 10 or 11 chain atoms the dimeric esters tended to predominate in oligomer mixtures obtained; ethylene adipate dimer has a 20-membered ring and a low proportion of monomer would be expected. However, analytical evidence suggests that more monomer than dimer was present in our autoclave distillate, probably because distillation conditions were milder than used by Carothers and Spanagel.

EXPERIMENTAL

Adipic acid (1495 g, 10.24 mol) and ethylene glycol (760 g, 12.26 mol) were charged to a stainless steel autoclave and heated with stirring beneath a steel fractionating column. An aqueous distillate (306 g) was obtained during 250 min as the melt temperature rose from 155° to 250°C. Antimony trioxide (1.2 g) was added as a suspension in glycol (5 ml) and the pressure was reduced to 0.6 mm over 17 min while the temperature was adjusted to 260°C. The melt was then stirred for 90 min at 260°C in the pressure range 0.6 to 3.5 mm to complete the polymerization, while a distillate (130 g) mainly composed of ethylene glycol was collected.

The clear colourless distillate was chilled overnight at 0°C and a white odourless crystalline solid was filtered off, washed with small volumes of glycol and water and dried in air. The dry product (1.7 g) had m.p 65°–66°C. By recrystallization at low temperature from methanol and then from trichloroethane the pure substance (I) was obtained with m.p 66.5°–67°C. By micro-analysis were found C, 56.0, 55.7%; H, 7.2, 7.2%: $(C_8H_{12}O_4)_n$ requires C, 55.8; H, 7.0%.

Analysis for hydroxyl groups by the pyridine/acetic anhydride method showed that both hydroxyl and carboxyl groups were absent or undetectable. Quantitative hydrolysis in a 1% solution of sodium hydroxide in 50% aqueous ethanol gave a figure of 85.5 for saponification equivalent; formula

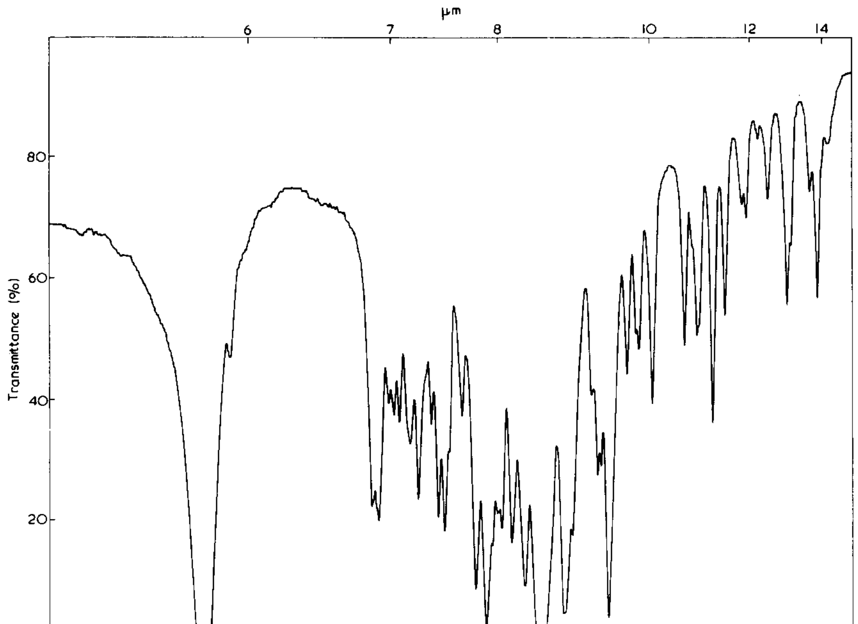

Figure 1 Infra-red spectrum of 1, 4, 11, 14–tetraoxacycloeicosan–5, 10, 15, 20-tetraone (I). The spectrum was obtained on a Beckmann IR 12 spectrometer using a pressed disc of 4 mg of sample in 400 mg of KBr

(I) requires 86.1. The infra-red spectrum (*Figure 1*) showed an ester carbonyl peak at 1740 cm^{-1} and no features indicating hydroxyl or carboxyl. The mass spectrum included the following elements of most significance; *m/c* 344 [M^+] (54%): 301 (8%); 285 (6%); 217 (26%); 173 (97%); 113 (49%); 99 (82%); 86 (52%); 55 (100%); 41 (45%).

The glycol mother liquor, after removal of substance (I) from the autoclave distillate, was sampled and saponified quantitatively in 1% sodium hydroxide solution in 50% aqueous ethanol. After correction for a small titrateable acidity, the filtrate sample was found to have a saponification equivalent of 1044, corresponding to a residual content of 8.25 wt % of esters calculated as cyclic oligomer. However, the solubility of pure cyclic dimer (I) in glycol is only of the order of 1%, suggesting that another substance was present in the mother liquor from (I).

After vacuum dehydration to still head temperature 54°C at 0.1 mm (water loss equal to 4.1% of sample weight), a sample of the filtrate (n_D^{25} 1.4315) was chromatographed on a column of silicone polymer OV–101 stationary phase on diatomite CLQ support at 200°C. Following the glycol peak was a major 'unknown' peak at a retention time of 1 min and a minor peak at 4.4 min, the apparent weight ratio of 'major' to 'minor' components being 10:1 approximately. The minor peak had the same retention time as samples of the purified cyclic dimer (I) added either in glycol or methanol solution. It was concluded that the major non-glycol component of the filtrate was an ester of vapour pressure rather lower than glycol but considerably higher than that of cyclic dimer (compare with Carothers cyclic monomeric tetramethylene succinate, isomeric with ethylene adipate, b.p 95°–96°C/2 mmHg). Evidence that this may be the cyclic monomer (*MW* 172) was given by the mass spectrum obtained from the glycol filtrate with the main relevant features: *m/c* 172 [M+], 142, 129 112 and 99.

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REFERENCE

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Partial chain coupling of anionically prepared polymers by air termination

L. J. Fetters and E. M. Firer
Institute of Polymer Science, The University of Akron, Akron, Ohio 44325, USA

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It is well recognized that certain anionic polymerization systems can yield chains possessing near monodisperse molecular weight distributions. In the course of work carried out in these laboratories over the last few years, we have observed that the air termination of chains bearing the lithium counterion can induce the formation of a 'dimer' of the parent species. The formation of such a species is, of course, not observed when chain termination is accomplished by proton transfer. This Note presents a summary of our findings which apparently show that termination by the atmosphere can convert an initially near monodisperse molecular weight distribution into one exhibiting distinct bimodal character.

EXPERIMENTAL

The anionic polymerizations were carried out under high vacuum conditions using the experimental techniques described elsewhere[1]. The monomers and solvents were purified by procedures outlined previously[1]. Purified sec-butyllithium was used as the initiator. Tetramethylethylenediamine (TMEDA) was purified by drying over calcium hydride and then exposure to dibutylmagnesium.

Gel permeation chromatography (g.p.c.) was used to examine the molecular weight distributions of homo and block copolymers prepared in this work. Tetrahydrofuran was the carrier solvent while the Waters differential refractometer was the detection instrument. Solvent flow rates of 1 and 0.25 ml/min were used.

Two different g.p.c. column arrangements were used in this work. These column sets were made up of 4 ft Styragel columns. The four column set had a porosity range of 5 x 10^3 to 7 x 10^5 Å while the five column set had a porosity range of 2 x 10^3 to 7 x 10^5 Å. Both column arrangements were such that no gaps in porosity existed within the range covered. Termination was accomplished by exposure of the chain ends to degassed methanol or the atmosphere.

All of the chromatograms with the exception of *Figure 2*, curve B were run on the 5 column set. Chromatograms in *Figure 1* (curves A and B) were run at the 0.25 ml/min flow rate while the remaining chromatograms were run at the rate of 1 ml/min. The number-average molecular weights of the polymers prepared in this work ranged from 8 x 10^4 to 1.2 x 10^5 g/mol.

RESULTS AND DISCUSSION

Apart from the usual possible impurities, the common terminating components in the air are water vapour, carbon dioxide and oxygen. Carbon dioxide has been shown[2] to lead to chain coupling involving polystyryl lithium while oxygen is claimed[3] to cause the coupling of organolithium compounds when TMEDA is present. Recently, g.p.c. results have appeared which show[4,5] that the anionically prepared Dow S-102 and S-109 polystyrenes contain high molecular weight components which seem to be near monodisperse in molecular weight. Some of these species seem to have molecular weights double that of the parent polymers.