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Characterization of metal-ion containing polyesters

A study of the glass transition behavior of poly(diethylene glycol-*co*-succinic acid) as a function of the effective molar mass

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Summary

The glass transition behavior of poly(diethylene glycol-*co*-succinic acid) (DEG-SA) and its complexes obtained in the reaction with MgO have been investigated. The number average molar mass ($\bar{M}_n$) of the DEG-SA samples prior to complexation was determined by titration of the terminal COOH groups. The glass transition temperature (T_g) was measured as a function of molar mass and Mg^{2+} ion content. The dependence of T_g on $\bar{M}_n$ obeyed the Fox-Flory relationship. Addition of increasing amounts of MgO to DEG-SA led to a gradual increase in T_g, and a decrease in the heat capacity change (Δc_p). This behavior is associated with complex formation between COO^- and Mg^{2+}. The decrease in Δc_p is a result of ion-ion and to a lesser extent ion-dipole interactions which lower chain mobility. The common limiting T_g value for the three DEG-SA samples at an Mg^{2+}/COO^- ratio of ca. 0.5 approaches $T_{g,\infty}$, which is the corresponding T_g of a polymer of infinite molar mass.

Introduction

Novel polymeric materials can be either synthesized in various types of polymerization reactions using appropriate monomer units, or made by chemical or physical modification of existing polymers. Unique engineered materials have been prepared by altering polymers containing functional groups with metal-containing reactants (1-3). The resulting reaction leads to intermolecular coordination bonds between the reactive groups of the macromolecule and the metal ions. Complexes of unsaturated polyesters are a particularly important example of great industrial relevance (4,5). Commercial applications include (6) preparation of polymer prepregs, filled polar polymers, composite materials, blend compatibilizers, polyester-based construction materials (e.g., concrete), etc .

In order to systematically design and predict the properties of new materials a thorough understanding of their behavior at the molecular level is essential. For example, it has been shown that the addition of small quantities (3 w/w%) of various metal oxides to some polyesters leads to drastic increases in melt viscosity (3). It was concluded that this increase was a result of ionic links

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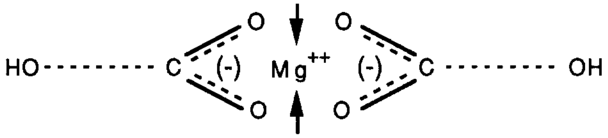
*To whom offprint requests should be sent which are formed between M^{2+} (M=bivalent metal) and terminal COO^- according to the following reaction:

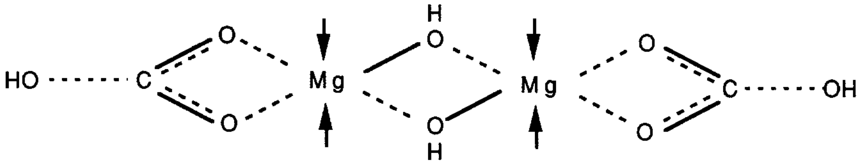
$$2\,[\sim COOH] + MgO \rightarrow M^{2+} + [COO^-]_2 + H_2O \qquad (1)$$

Metal oxides such as MgO, ZnO, and CaO with base-anhydride character are the most effective chelating agents. Monitoring of the terminal carboxyl group by Infrared Spectroscopy has shown (7) that the carboxylate complex is favored at an Mg^{2+}/COO^- ratio of ≈ 0.5:



(I)

where the dashed horizontal line represents the polyester chain. At one equimolar ratio the formation of a carboxylato-hydroxo complex becomes favorable:



(II)

As a result of complex formation polyester chains become linked and the effective molar mass of the polymer increases. The complexed Mg^{2+} has two additional unoccupied coordination sites indicated by the arrows in scheme **(I)** and **(II)**. The sequence of donor strengths for the other polar groups that can occupy these sites is as follows (8): H_2O > terminal OH > ester carbonyl. Thus, Mg^{2+} ions act as effective "polar branching" points. By varying the concentration of Mg^{2+} the branching density and the effective molar mass can be varied.

This article presents results on the characterization of the glass transition behavior of poly(diethylene glycol-*co*-succinic acid) (DEG-SA) and its complexes with Mg^{2+}. In a previous article (9) we have published a similar study on poly(diethylene glycol-*co*-fumaric acid).

Experimental

Synthesis of the saturated polyesters of diethylene glycol (DEG) and succinic acid (SA) was achieved by a melt polycondensation at 180 °C using a molar ratio of DEG/SA of 1.02. Complexes of DEG-SA/Mg^{2+} were prepared by adding MgO (Fluka 63091, purity > 98 %) in the form of a fine powder to DEG-SA diluted in toluene (10 w/w%). The slurry was then thoroughly mixed (15 min.)

until the MgO was well dispersed. The mixtures were allowed to react over a period of 2-5 days at 60 ^{o}C and subsequently pumped under vacuum until all toluene was removed. Thermogravimetric analysis was used to confirm the absence of the solvent.

The number average molar mass ($\bar{M}_n$) of the samples was determined by end group titration and verified by ebulliometry for the sample DEG-SA38. Titration of terminal COOH was performed in tetrahydrofuran using NaOH and bromothymol blue as the indicator. If the principle of equal reactivity (10) during the condensation reaction is fulfilled then the probability of having carboxylic or alcoholic chain ends is equal and COOH titration results in $\bar{M}_n$ values. A summary of the titration results and sample codes is displayed in Table I. Since ($\bar{M}_n$) values obtained by titration and ebulliometry for DEG-SA38 agreed to within ± 2 %, the procedure was deemed satisfactory.

Table I
$\bar{M}_n$ and T_g values of the various polyesters.

DEG-SA*	$\bar{M}_n$ titration	T_g
128	440	-49.6
82	681	-42.5
57	985	-38.2
53	1062	-37.6
37	1535	-34.7

* The numbers in column 1 correspond to the acid number (mg KOH/g PES) of each polyester and is used to identify the samples.

Glass transition measurements were performed on a Perkin-Elmer DSC-7 differential scanning calorimeter which was equipped with a dry box assembly using N_2 as the purge gas and a liquid nitrogen subambient accessory. DSC experiments were performed at a scan rate of 10 $^{o}C/min$. A Brookfield Programmable Rheometer model DV-III was used to measure the melt viscosity of the various polyester samples. The calibration of the instrument was verified by comparing the quoted viscosity values of a standard silicon oil (HT30'000, Brookfield Eng. Labs Inc.) at three temperatures with measured values. In all cases agreement was better than ± 2 %.

Results and Discussion

The physical property which undergoes the most drastic change as a result of the addition of MgO to the polyester DEG-SA is the melt viscosity (η). The increase in η of DEG-SA53 measured at 110 °C as a function of the molar ratio of Mg^{2+}/COO^- is shown in Figure 1. The viscosity behavior can best be explained in terms of the types of complex which prevail at a given Mg^{2+} content (3). Prior to exceeding a Mg^{2+}/COO^- ratio of 0.25 an excess of donor ligands exists in the system. At these concentrations individual "polar branching" points are not joined through ion-dipole interactions. As the Mg^{2+} content is gradually increased a growing number of the additional coordination sites are occupied by terminal OH groups from neighboring complexes. The linking of individual polar branching points leads to an abrupt increase in the melt viscosity. As the concentration of complex (II) grows ester units play a greater role in extending the density of the ionic network even further.

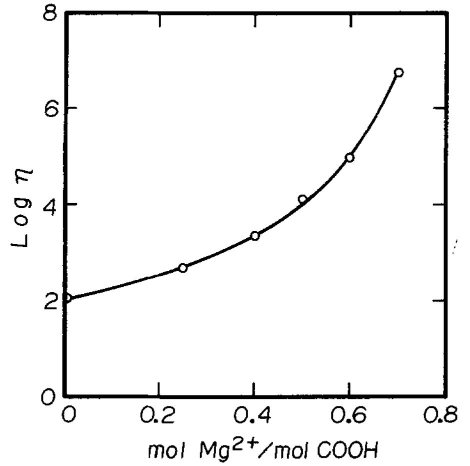


Figure 1. Plot of the log melt viscosity (mPa s) versus ion concentration for DEG-SA 53 complexes at a temperature of 110 °C.

For macromolecules with a low degree of polymerization (ca. 100-300) (11) the value of the glass transition temperature T_g depends strongly on the molar mass of the polymer. The dependence of T_g on the reciprocal number average molar mass $1/\bar{M}_n$ for MgO-free DEG-SA is shown in Figure 2. The behavior is

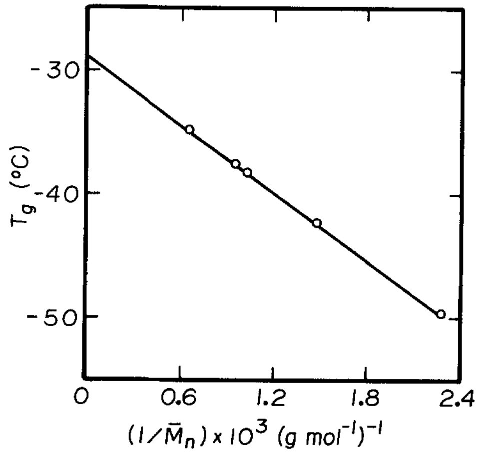


Figure 2. Plot of the glass transition temperature of DEG-SA against the reciprocal of the number average molar mass.

linear and can be described by the Fox-Flory relationship (12) which is based on the free volume theory:

$$T_g = T_{g,\infty} - k / \bar{M}_n \qquad (2)$$

where $T_{g,\infty}$ is the glass transition temperature in the limit of infinite molar mass and k is a constant which is proportional to the excess free volume per chain end. For DEG-SA a value of $T_{g,\infty}$ of -28.9 °C was obtained.

Typical DSC traces (the measured heat flow vs. temperature) for DEG-SA53 in the absence and complexed with 0.5 equimolar Mg^{2+} are illustrated in Figure 3. Tangents were fitted to the measured DSC profiles within specified limits to determine the onset and endset of the glass transition, while T_g is the temperature at which the heat capacity of the sample is midway between the rubbery and glassy states (i.e. between the onset and endset heat capacity values of the transition).

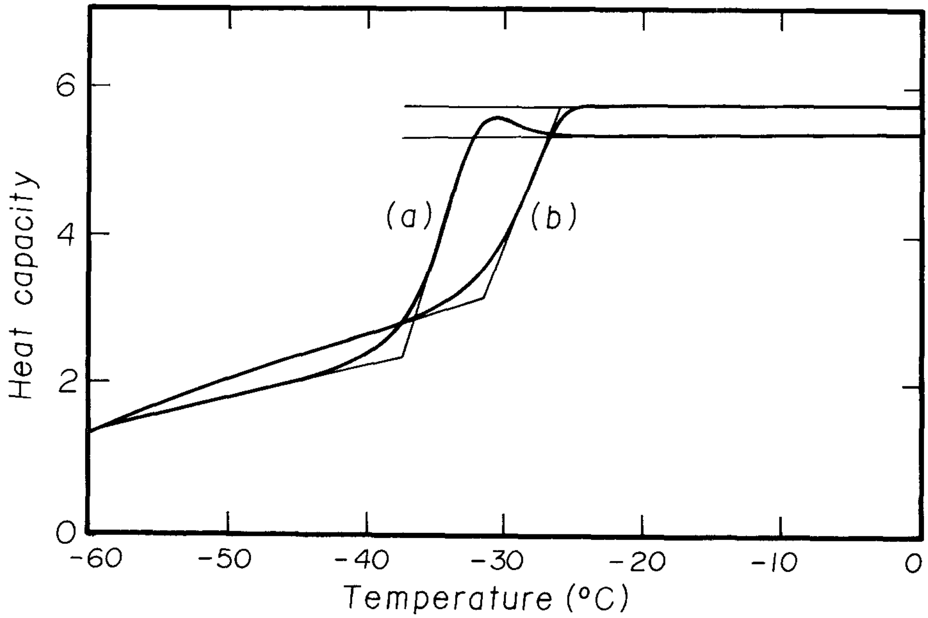


Figure 3. DSC thermograms of DEG-SA37 for a heating rate of 10 °C/min.
(a): pure sample: T_g=-34.7 °C;
(b): complexed with 0.5 equimolar Mg^{2+}: T_g=-28.5 °C.

The change in T_g for three samples with different $\bar{M}_n$ as a function of Mg^{2+} concentration was also investigated and the results are plotted in Figure 4. The glass transition temperature increased with greater Mg^{2+} content and reached a limiting value of -28.6 °C for all three samples at a molar ratio of

Mg^{2+}/COO^- of 0.5. This value is only 0.3-0.4 °C lower than $T_{g,\infty}$ which is displayed as a dashed line in Figure 4. Using eq. (3) with the parameters determined from the plot shown in Figure 2, the limiting T_g value of -28.9 °C corresponds to an effective molar mass of approximately 30,000 g mol^{-1}.

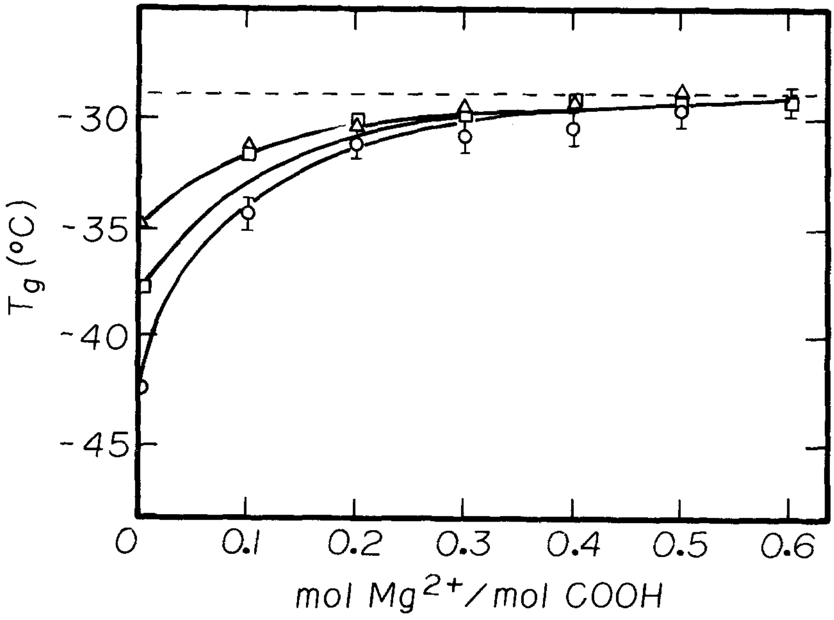


Figure 4. Plot of the glass transition temperature vs. the molar ratio of Mg^{2+}/COO^-. (o) DEG-SA82; (□) DEG-SA53; (Δ) DEG-SA37.

The rise in T_g with increasing Mg^{2+} concentration is attributed to the formation of intermolecular links formed via ionic and polar interactions [see the complexes (**I**) and (**II**)]. It is important to mention that the formation of this ionic network, and the increase in T_g, is accompanied by an increase in the cohesive energy density of ion containing polyesters. This conclusion is based on an analysis of the pressure-volume-temperature phase diagram of complexes of poly(diethylene glycol-*co*-succinic acid) with Mg^{2+}. Detailed results of this study will be published elsewhere (13).

The difference in the heat capacity values between the onset and endset temperatures of T_g (see Figure 3) corresponds to the change in the heat capacity (Δc_p) associated with the transition. The DSC curves shown in Figure 3 have the following characteristics: for pure DEG-SA53 Δc_p= 0.969 $Jg^{-1}K^{-1}$; while for DEG-SA53 complexed with 0.5 equimolar Mg^{2+} Δc_p= 0.810 $Jg^{-1}K^{-1}$. The decrease in Δc_p as a function of the molar ratio of Mg^{2+}/COO^- is illustrated in Figure 5. All three polyesters display a similar trend; i.e. an increase in the metal ion content produces a reduction in Δc_p. It is well known that the heat capacity c_p is proportional to the number of degrees of motional freedom (14).

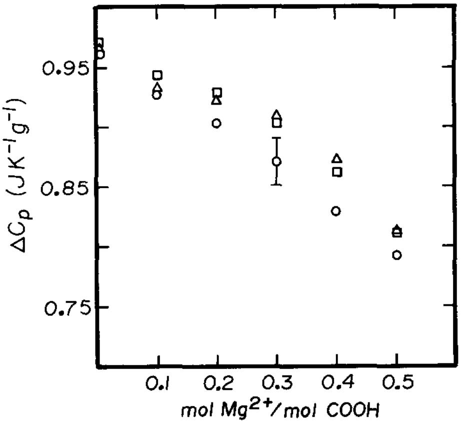


Figure 5. Heat capacity change at T_g vs. the molar ratio of Mg^{2+}/COO. (o) DEG-SA82; (□) DEG-SA53; (Δ) DEG-SA37.

The observed decrease in Δc_p means that ion formation leads to a decrease in the number of motional degrees of freedom. This is a result of ionic links between end groups of macromolecules as well as intermolecular ion-dipole connections which restrict segmental mobility.

Acknowledgement

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