Polymerization of Ethylene Terephthalate Cyclic Oligomers with a Cyclic Dibutyltin Initiator†

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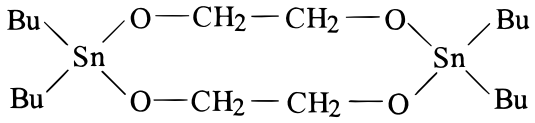
ABSTRACT: To produce high-performance poly(ethylene terephthalate) (PET) composites from the polymerization of ethylene terephthalate cyclic oligomers (ETCs) prepared from PET waste, the viscosity, thermal stability, and crystallization of ETC melts were investigated, and ETC melt was polymerized with cyclic dibutyltin initiator (cyclic stannoxane **1**). The melt viscosity of ETCs at 295 °C where all ETCs can be melted was about 30 cP initially. The viscosity of the completely molten ETCs remained sufficiently constant at 295 °C to allow time for infusion into large composite preforms, and nearly all of the ETC molten sample remains a liquid for tens of seconds when quenched to the most desirable polymerization/solidification temperature. From the polymerization and crystallization results, it was found that the optimum polymerization temperature is approximately 230 °C. PET polymerized at this temperature had enough crystallinity for a good composite matrix; however, the molecular weights of such PETs were too low to form sufficiently strong tough matrices for composites; this is probably due to small amounts of impurities which produce low molecular weight PET and inadequate thermal stability of the cyclic stannoxane **1** initiator at this temperature.

Introduction

The application of thermoplastic resins in high-performance composites has been limited by the high melt viscosities of such polymers relative to the viscosities of thermosetting resins. This adds considerably to the difficulty and expense of the fabrication of thermoplastic composite parts. Especially, in the case of polyarylate, its lower solubility and higher melting temperature have prevented its use in such applications. As an alternative to these problems, the polymerization of reactive cyclic oligomers as low-viscosity precursors to thermoplastic resins has received considerable attention in recent years, and many researchers have developed reliable methods for preparing cyclic oligomers from thermoplastic resins and processing such oligomers.[1−14]

On the other hand, during the past few decades the growth in the commercial use of poly(ethylene terephthalate) (PET) has brought with it the increasing problem of its reuse. In previous research[15] we established a method for PET recycle by converting it into ethylene terephthalate cyclic oligomers (ETCs). The resultant materials are valuable chemical intermediates for the economical manufacture of matrices for high-performance thermoplastic composites. To be suitable for the fabrication of thermoplastic composites, ETCs must be subsequently melted, infused easily into fiber composite preforms, polymerized rapidly in place, and the PET so formed crystallized within minutes at the same temperature as that at which it was polymerized.

In this research, we tested the possibility of producing high-performance thermoplastic composites by using ETCs as low-viscosity precursors. First, we investigated the viscosity and thermal stability of ETC melts and the crystallization of molten ETCs after quenching to polymerization temperature. Second, we polymerized ETCs with cyclic stannoxane **1**,[13,14] which is known to be an effective initiator for the polymerization of cyclic ester oligomers, and analyzed the molecular weight and crystallinity of the resultant PETs.



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Experimental Section

General Information. High-pressure liquid chromatography (HPLC) analysis was performed to confirm the presence of remaining linear oligomers using a Waters 600 liquid chromatograph equipped with an ultraviolet detector (wavelength 254 nm) and a Supelco LC-Si 5 μm column. The chromatograph was run at a flow rate of 1.0 mL/min at 25 °C. The solvent was 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP)/chloroform (1/20 v/v), and the eluent was ethanol/chloroform (4/96 v/v). The detection of linear oligomers by this analysis was already discussed in our previous research.[16] The content of Sb in ETCs was measured with a Direct Reading Echelle inductively coupled plasma (ICP) spectrometer (Leeman Labs Inc., DRE). The melt viscosity of ETCs at 295 °C has been measured by using a Brookfield viscometer. The number-average molecular weight (M_n) of thermally polymerized ETCs during the melting at 295 °C was calculated from values of intrinsic viscosity [η] using the Berkowitz[17] equation: $M_n = 3.29 \times 10^4[\eta]^{1.54}$. The intrinsic viscosity measurement was done at 25.0 ± 0.01 °C and a polymer concentration of 0.25% in 60/40 w/w phenol/1,1,2,2-tetrachloroethane. Following Berkowitz, the intrinsic viscosity of each sample was calculated using the Solomon−Ciuta[18] equation for a single-point measurement: $[\eta] = [2(\eta_{sp} - \ln \eta_{rel})]^{0.5}/c$. The solution viscosity of PET polymerized with cyclic stannoxane **1** was measured at 20.0 ± 0.01 °C and a polymer concentration of 0.25% in HFIP. The intrinsic viscosity of each sample was also calculated using the Solomon−Ciuta equation for a single-point measurement. A Perkin-Elmer differential scanning calorimeter (DSC-7) was used to study the crystallization behavior. The thermal stabil-

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† This paper is dedicated to Dr. Karel Dusek on the occasion of his 65th birthday.

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ity of cyclic stannoxane **1** was measured by a Perkin-Elmer thermogravimetric analyzer (TGA-7) under a nitrogen atmosphere at a heating rate of 10 °C/min.

Production of ETCs via Ring/Chain Equilibration in Dilute Solution (Cyclodepolymerization). The cyclodepolymerization method[15,19] was used to prepare the ETCs used here. A 2 gal reactor was charged with about 50 g of PET ($M_n \approx 20\,000$) and 5.5 L of *o*-dichlorobenzene to produce a solution 0.05 M in ethylene terephthalate residues. The solution was heated to 240 °C with 3 mol % of titanate catalyst. After 1.5 h the product solution was cooled to 100 °C to induce the precipitation of any unreacted linear polymer. The latter was then removed by filtration. The cyclic oligomers were subsequently recovered from the resulting filtrate by vacuum evaporation of the solvent, followed by recrystallization from hexane and filtration. Additionally, remaining linear oligomers were filtered off with dichloromethane. The yield was 50%. ETC trimer is the most predominant cyclic, and its content is 30 wt %. Small amounts of linear oligomers or impurities (peak area 7.29%) were detected in the HPLC analysis. The ETCs thus prepared are a distribution of oligomeric species displaying a broad melting range, the uppermost end of which lies at 290 °C. This melting temperature resulted from the significant depression of the melting temperatures of the high-melting oligomers by the presence of the lower-melting ones.

Preparation of Cyclic Dibutyltin Initiator (1,1,6,6-Tetra-*n*-butyl-1,6-distanna-2,5,7,10-tetraoxyacyclodecane, Cyclic Stannoxane 1). Dibutyltin oxide (29.9 g, 0.12 mol) and ethylene glycol (7.54 g, 6.67 mL, 0.12 mol) were charged into a 500 mL flask containing distilled toluene (63 mL). The flask is fitted with a sidetrap condenser system to collect distillate and return overflow to the reaction vessel. The contents were slowly heated to reflux, upon which the dibutyltin oxide dissolved. The reaction is finished when the water level in the trap appears to be constant. The cold reaction product was covered lightly and allowed to dry overnight followed by a vacuum-drying for 24 h at 50 °C. Anal. $C_{20}H_{44}Sn_2O_4$ (585.95), $T_m = 223-229$ °C.[20-22]

Polymerization of ETCs. The polymerization of ETCs was conducted with cyclic stannoxane **1** which is capable of producing a coordinated ring expansion polymerization. A 0.5 g sample of ETCs dried in a vacuum oven at 80 °C for 12 h was introduced into a vial. The ETCs were melted at 295 °C for 1.5 min, quenched to a predetermined polymerization temperature, immediately mixed with cyclic stannoxane **1**, and then polymerized for 10 min.

Results and Discussion

Melt Viscosity of the ETCs. An important area of utilization of ETCs will be in reaction injection molding (RIM) and composite reaction injection molding (CRIM). Because of the low viscosities of the starting materials, RIM and CRIM processes are attractive in that they afford the opportunity to produce large parts with complex shapes. To be suitable for a RIM process, molten ETCs must be easily pumped into glass fiber mats and textiles and reacted in situ to form high polymer that crystallizes quickly and, ideally, at the same temperature as that of the infusion step.

The melt viscosity of ETCs at 295 °C measured by a Brookfield viscometer is about 30 cP initially. For comparison, the viscosity of ethylene glycol at room temperature is 20 cP. More significant is a comparison of the melt viscosity of ETCs at 295 °C with that of butylene terephthalate cyclic oligomers (BTCs) measured at a temperature (190 °C) that allows for BTCs use in the fabrication of large structures by a CRIM process: At 190 °C the BTC melt viscosity is 20 cP. Thus, the ETC viscosity at 295 °C—where the trimer is completely molten—is only 50% greater than that of

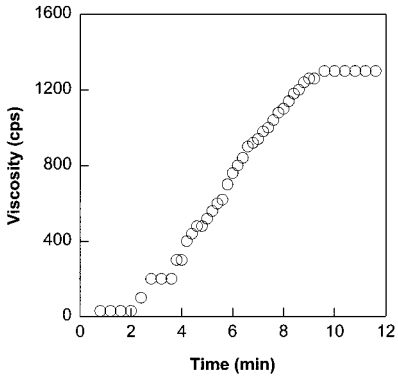

Figure 1. Dependence of the melt viscosity of neat ETCs on time at 295 °C.

BTCs at temperatures that allow for easy infiltration of the BTCs into large glass preforms. This low viscosity is a key finding vis-à-vis the facile use of ETCs as-made in CRIM and other composites manufacturing processes. Moreover, the viscosity of the completely molten ETCs—with no initiator added—remains sufficiently constant at 295 °C to allow time for infusion into large composite preforms: Figure 1 shows the change of melt viscosity of the ETCs with time at this temperature. The viscosity was 30 cP up to 2 min. After this a linear increase with time was seen, probably due to polymerization triggered by impurities. Goodman and Nesbitt[23-25] suggested that the initiating substances in the polymerization of ETCs may be water, or mono- or polyhydric alcohols, or any other compound providing molecular fragments.

Thermal Polymerization of Molten ETCs. The optimum procedure for using ETCs for manufacturing CRIMs is believed to be a bithermal one in which the ETCs are held in the molten state in a reservoir at 290 °C, and periodically a portion of this melt is passed through a so-called mix head. In this mixing device a controlled amount of the polymerization initiator is injected at a controlled rate while the mix is being injected into the composite preform. In this context an important characteristic of the ETCs is their stability vs thermal polymerization or thermal degradation.

Thus, a brief investigation of the thermal stability of neat ETCs has also been conducted. This was carried out by (a) heat-treating samples of neat ETCs (i.e., ETCs to which no polymerization initiator has been added) for various periods of time at 295 °C, (b) measuring the molecular weight of a portion of each specimen, and (c) extracting with 1,4-dioxane (which could dissolve only ETCs) and weighing the amount of unreacted ETCs from a second portion of each heat-treated sample.

Figure 2a shows the change of the number-average molecular weight M_n of ETCs and Figure 2b the increase of PET content, both with time of thermal exposure at 295 °C. As seen in Figure 2, heating for more than 2 min has caused conversion of some of the ETCs to PET. Goodman and Nesbitt[23-25] separated individual cyclics from ETCs extracted from PET chip and successfully polymerized them with antimony trioxide (Sb_2O_3) to high molecular weight PET. This may have occurred because of residual Sb_2O_3 used for the original polymerization of the PET. The content of Sb in ETCs measured using an ICP spectrometer was 0.2 wt %. M_n is seen from Figure 2 a to have risen abruptly after 3 min of heat treatment, finally reaching a value of 5000 g/mol before leveling off. Afterward an increasing

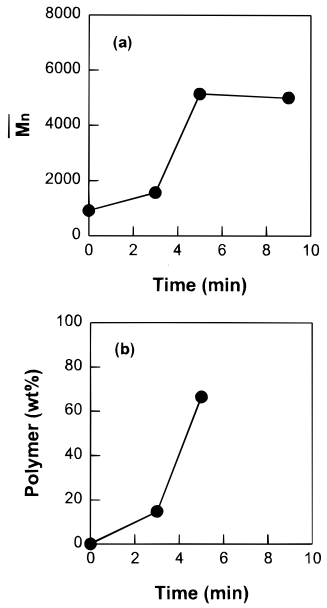

Figure 2. Dependence of the polymerization of ETCs containing no added initiator on time at 295 °C: (a) number-average molecular weight M_n, (b) polymer content.

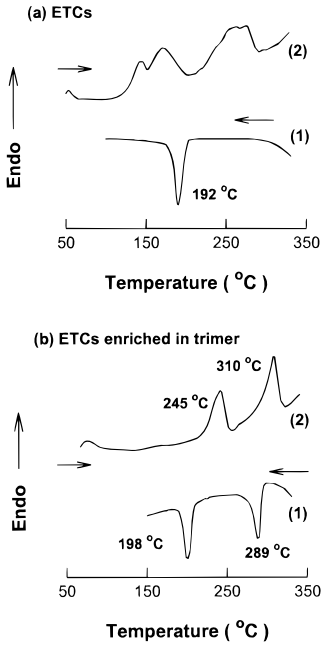

Figure 3. DSC scans of (a) ETCs as synthesized and (b) trimer-enriched ETCs in each case after heating to 340 °C. Scan 1: cooling scan at 10 °C/min; scan 2: heating scan at 20 °C/min after scan 1.

discoloration of the ETCs was seen, suggesting the beginning of thermal degradation: If indeed degradation was occurring, it could account for the leveling off of molecular weight. Figure 2b shows that more than 60 wt % of the neat ETCs underwent ring-opening polymerization in 5 min at 295 °C. (It is worth emphasizing however that in an actual industrial RIM process the ring-opening polymerization of the ETCs before the initiator is added would not be a problem because the total time for processing of the ETCs would not exceed 1 min.)

Crystallization of Molten ETCs. For the PET to crystallize reasonably fast after polymerizing with an initiator, the reaction temperature should be maintained at least 20 °C below the polymer T_m (ca. 260 °C). However, as noted before, the ETCs as-synthesized have a mix of oligomeric species melting out over a wide range ending at 290 °C. Thus, for any isothermal polymerization and crystallization process to succeed, unfractionated ETCs will have to be melted at ca. 295 °C, quenched to ca. 240 °C, mixed with initiator, and injected into the composite preform before crystallization of the unreacted ETCs occurs to any appreciable degree. Therefore, the time for crystallization to start after molten ETCs have been quenched from ca. 295 to 240 °C is a characteristic critical to any practical CRIM process. For this reason an assessment of the crystallization behavior of quenched ETCs in this temperature range has been started. DSC scans are shown in parts a and b of Figure 3 respectively for ETCs as-synthesized and ETCs deliberately enriched in trimer by using solubility difference in cyclic species with acetone and monochlorobenzene,[23,24] the major oligomer in the distribution having the highest melting point. Each specimen was first heated at 20 °C/min to 340 °C and then cooled to 30 °C at 10 °C/min, which is a relatively slow cooling rate. During this cooling process ETCs as-synthesized showed no exotherm that could be associated with trimer crystallization: This behavior stands in contrast to that of the trimer-enriched specimen which, on cooling, displays a crystallization exotherm at about 289 °C. Thus, as-synthesized ETCs could easily

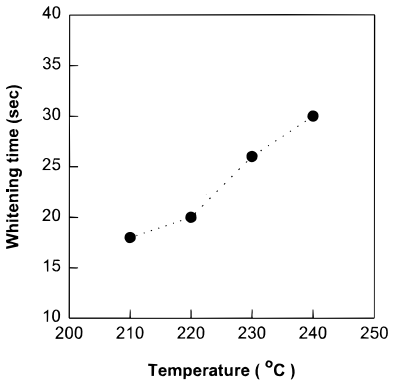

Figure 4. Whitening time of ETCs first melted at 295 °C for 90 s vs the subsequent crystallization temperature.

be quenched to below 200 °C and remain liquid during the process. This is possible presumably because the trimer in the as-synthesized ETCs is present at a lower concentration which makes its crystallization more difficult.

Figure 4 shows the time for whitening of molten ETC samples (i.e., the whitening due to ETCs crystallization) as a function of the hold temperature (i.e., that temperature to which the specimen was quenched after melting at 295 °C for 90 s). At lower hold temperature, the whitening time of the ETCs is smaller. Importantly, at 240 °C—the polymerization/polymer-crystallization temperature currently projected to be the optimum one for the eventual CRIM process—whitening did not become substantial within 30 s. In short, most of the ETC molten sample remains a liquid for tens of seconds when quenched to the most desirable reaction/solidification temperature. This delay should make possible a process in which quenched ETCs are isothermally mixed with a liquid initiator, injected into a preform, polymerized, and the resultant PET crystallized in a process in which the polymerization and PET crystallization steps can be carried out at a single temperature.

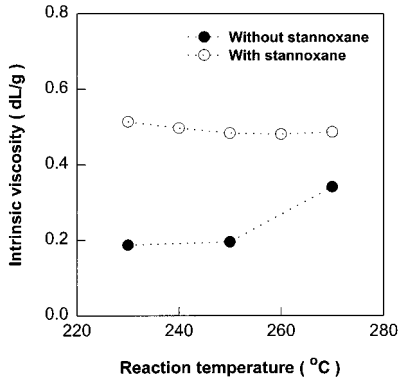

Figure 5. Effect of reaction temperature on the polymerization of ETCs with 0.5 mol % and without cyclic stannoxane **1**.

Polymerization of ETCs. Butyltin alkoxides and phenyltin alkoxides have been reported to be efficient initiators of the ring-opening polymerizations of various lactones and lactides.[26−28] The reactivity of the initiators increases with the number of alkoxide groups attached to the tin atoms, and it decreases with increasing bulkiness of the alkoxide groups. Butyltin alkoxides are also efficient transesterification catalysts for noncyclic ester groups and may cause intensive backbiting degradation of polylactones at elevated temperature.

In this research, the polymerization of ETCs was conducted with cyclic stannoxane **1** which is a cyclic dibutyltin alkoxide initiator capable of producing a coordinated ring expansion polymerization.[14,29−31] During the polymerization, the Sn−O link coordinates with a carbonyl link in the PET, incorporating the initiator into the cyclic oligomer and expanding the ring while maintaining its cyclic structure. Therefore, the polymer obtained in this research may be macrocyclic PET.

ETCs were melted at 295 °C for 1.5 min, quenched to a predetermined polymerization temperature, immediately mixed with a small amount of cyclic stannoxane **1**, and then held at this temperature for 10 min to polymerize the sample. The molecular weight of the resulting polymer is primarily dependent on the molar ratio of monomer/initiator (M/I). To study the effect of M/I ratio, the polymerization of ETCs was conducted with 0.3, 0.5, and 0.7 mol % cyclic stannoxane **1** at 240 °C for 10 min. The resulting intrinsic viscosities were 0.52, 0.50, and 0.45 for 0.3, 0.5, and 0.7 mol % cyclic stannoxane **1**, respectively. Figure 5 shows intrinsic viscosities for PETs obtained at different polymerization temperatures with 0.5 mol % and without cyclic stannoxane **1**. For comparison, the intrinsic viscosity of a commercial linear PET purchased from Aldrich Co. is 1.05 dL/g. The intrinsic viscosities of PET obtained at various reaction temperatures were about 0.5 dL/g irrespective of the reaction temperature. On the basis of a comparison with the intrinsic viscosities of the Aldrich Co. PET, it appears that the intrinsic viscosities of these PETs are lower than those of PET resins we expect would be able to form the matrices of tough thermoplastic composites.

The remaining ETCs after polymerization at 230 °C for 10 min were Soxhlet extracted with 1,4-dioxane for 24 h. Ten weight percent of oligomers was extracted. However, it was found from HPLC analysis that the extract contains large amounts of unknown linear oligomers (peak area 55%). This analysis shows that unreacted and re-formed ETCs produced by a backbiting reaction in the macrocyclic structure exist in the resulting PET.

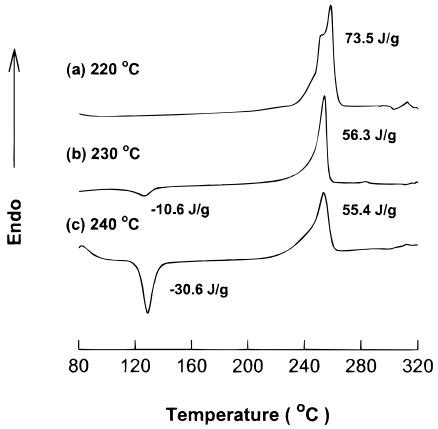

Figure 6. DSC scans of PET polymerized at indicated temperature at a heating rate of 20 °C/min.

Crystallization of PET at the Reaction Temperature. The degree of crystallinity (X_c) of the PET is directly related to the polymerization time and temperature of the ETC melt. The crystallization during the polymerization of ETCs at 220, 230, and 240 °C for 10 min was evaluated by measuring the heat of fusion (ΔH_f) of the PET specimens that underwent these isothermal polymerizations and crystallizations. Following each of these isothermal preparations, the specimen was quenched in ice water. Figure 6 shows DSC scans of PET polymerized and quenched as described above. As can be seen, ΔH_f varies with the reaction temperature. The calculated X_c of PET, obtained by taking the value of 140.1 J/g as ΔH_f of 100% crystalline PET,[32] is 52.5, 32.6, and 17.7% for the samples polymerized at 220, 230, and 240 °C, respectively. The DSC heating trace of PET polymerized at 220 °C shows the presence of small amounts of cyclic trimer as evidenced by the small endotherm at about 310 °C. This indicates that crystallization of cyclic oligomers, especially cyclic trimer, occurs before they have all polymerized. In the case of PET polymerized at 240 °C, it is found that the reaction temperature is too high to crystallize PET to completion within the 10 min the sample was held at this temperature. The optimum combination of quench temperature and hold time at the quench temperature—optimum in terms of PET molecular weight and level of crystallinity—has still to be determined precisely. However, from the above polymerization and crystallization results, we can conclude that the optimum reaction/crystallization temperature is in the neighborhood of 230 °C.

Intrinsic Viscosity and Crystallinity of PET Polymerized at 230 °C. We have carried out the polymerization of ETC melts with 0.5 mol % cyclic stannoxane **1** at 230 °C for various lengths of reaction time. Figure 7 shows the dependence of the intrinsic viscosity of PET polymerized at 230 °C on reaction time. Intrinsic viscosity of PET rose abruptly early in the polymerization, climbed more slowly after the first 30 s, and reached a value of 0.51 dL/g after 10 min. This result also reflects the change of melt viscosity of ETCs with 0.5 mol % cyclic stannoxane **1**. The crystallization during the polymerization of ETCs at 230 °C—which is at least 30 °C below the melting temperature of crystalline PET—was evaluated as a function of polymerization time by measuring ΔH_f of the PET specimens. To

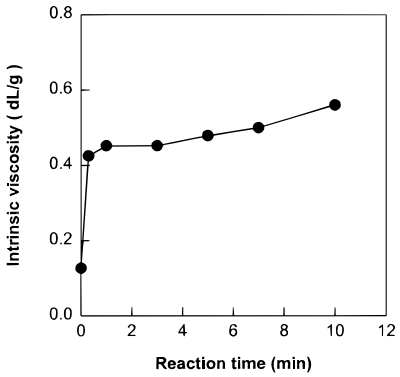

Figure 7. Dependence of intrinsic viscosity of PET polymerized with 0.5 mol % cyclic stannoxane 1 at 230 °C on reaction time.

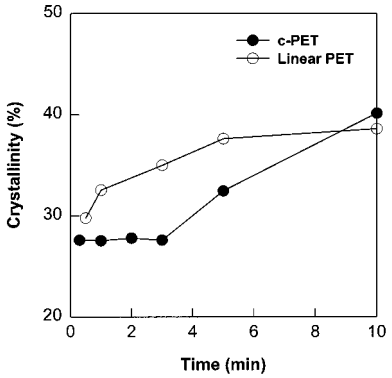

Figure 8. Time dependence of the crystallization of linear PET quenched from 295 to 230 °C and PET polymerized at 230 °C with 0.5 mol % cyclic stannoxane **1** (c-PET).

compare the crystallization of PET polymerized with conventional PET, specimens of this material were quenched from the melt and isothermally crystallized in a procedure as comparable as possible to that for the PET specimens. Following each of these isothermal crystallizations, the resulting polymer specimens were quenched in ice water. Figure 8 shows the calculated X_c of PET polymerized and conventional PET specimens as described above. Because the PET polymerizations were carried out at such a low temperature (i.e., at such a large degree of undercooling), a critical combination of chain concentration and chain molecular weight was reached at which nucleation began. Because of the large undercooling, crystallization took place rapidly once nucleation had begun. Values of X_c of PET specimens did not begin to increase until 3 min had elapsed after the samples had been brought up to 230 °C but then rose slowly with further reaction time. However, in the case of conventional PET, X_c began to increase rapidly immediately after quenching to 230 °C, then slowed, and finally leveled off after 5 min.

Thermal Stability of Cyclic Stannoxane 1. In the course of this research the ultimate utility of the cyclic stannoxane **1** initiator for ETCs has come under considerable scrutiny. Even though at 230 °C and 10 min reaction time we obtained PET with sufficient crystallinity (32.6%), the molecular weight of the polymer produced—as judged by its intrinsic viscosity (0.51 dL/g)—is probably not high enough to form a sufficiently tough composite matrix. We suspect that the lower intrinsic viscosities of these PET specimens and the lack of dependence of these viscosities on the polymerization temperature may be due to the thermal instability of

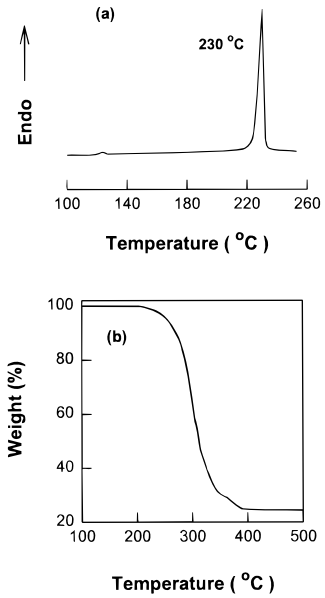

Figure 9. Thermal analysis of cyclic stannoxane **1**: (a) DSC, (b) TGA.

cyclic stannoxane **1** initiator used at the temperature of our polymerizations. Support for this suspicion is found in Figure 9, which shows a scanning calorimetry trace and a thermogravimetric analysis trace obtained on samples of the cyclic stannoxane **1** initiator. Cyclic stannoxane **1** starts to lose weight below its melting temperature. Moreover, it was clearly observed that cyclic stannoxane **1** quickly starts to degrade to dark brown material when melted at 230 °C under a nitrogen atmosphere. The cyclic stannoxane **1** initiator is a dimeric associated species in the solid state but dissociates at higher temperatures and forms an equilibrium with the monomeric five-membered ring.[30] It was reported that cyclic stannoxane **1** is seen to lose about 12% of its weight within 30 min when held isothermally at 220 °C.[33] In this study, ETCs and cyclic stannoxane **1** were mixed by stirring at high temperatures so that it is considered that some of them were thermally degraded before starting the polymerization and polymerization was also limited by their insufficient thermal stability.

Conclusion

ETCs prepared by cyclodepolymerization constituted a distribution of oligomeric species displaying a broad melting range, the uppermost end of which lies at 290 °C. The melt viscosity of ETCs at 295 °C was about 30 cP initially. The viscosity of the completely molten ETCs with no initiator added remained sufficiently constant at 295 °C, and nearly all of the ETC molten sample remained a liquid for tens of seconds when quenched to the most desirable polymerization/solidification temperature. It was found from the polymerization carried out with 0.5 mol % cyclic stannoxane **1** and the crystallization results that the optimum polymerization/crystallization temperature is in the neighborhood of 230 °C. Although the PET polymerized at 230 °C was sufficiently crystalline to form a thermally resistant and solvent-resistant composite matrix, the molecular weights of these PETs judged by their intrinsic viscosities were too low to form composite matrices having acceptable strength characteristics. This limitation is probably due to small amounts of impurities which polymerize ETCs

to low molecular weight PET and the insufficient thermal stability of cyclic stannoxane **1** at this temperature. However, we also believe that more rigorous purification of ETCs and replacement of the cyclic stannoxane **1** initiator with one from another class of cyclic ester polymerization initiators, a class known to have greater thermal stability (i.e., certain organotitanates), will produce PETs with higher molecular weights.

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