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Effects of Catalyst and Polymerization Temperature on the In-Situ Polymerization of Cyclic Poly(Butylene Terephthalate) Oligomers for Composite Applications

Amiya R. Tripathy,[†] Aadil Elmoumni,[‡] H. Henning Winter,[†,‡] and William J. MacKnight*[,†]

Department of Polymer Science & Engineering, and Department of Chemical Engineering, University of Massachusetts Amherst, Massachusetts 01003

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ABSTRACT: The in-situ polymerization at different polymerization temperatures, and the crystallization behavior of cyclic poly(butylene terephthalate) oligomers, using various process-suitable catalysts, are investigated in this paper. The choice of the catalyst has a large effect on the polymer conversion and the time required for polymerization, as studied by light transmittance measurements. The resulting polymer is characterized by GPC for molecular weight and polydispersity and by WAXD and DSC for crystal morphology. SALS is used for in-situ observation of the melt crystallization during polymerization.

1. Introduction

The recently developed macrocyclic polyester oligomers such as cyclic poly(butylene terephthalate) (c-PBT) have unique properties such as low melt viscosity (0.017 Pa s, water-like) and the capability of rapid polymerization virtually isothermally and without the evolution of low-molecular-weight byproducts.[1−3] These properties make them attractive matrix materials for engineering thermoplastic composites: in particular, the low viscosity of c-PBT allows easy impregnation of dense fibrous prepregs followed by polymerization to poly(butylene terephthalate) in the presence of transesterification catalysts.[4−6] The usual catalysts employed for the polymerization of c-PBT oligomers include various organotin compounds and titanate esters.[7−10] To broaden the application range of c-PBT oligomers, it is worth exploring the versatility of these catalytic systems and sufficiently understanding them so that they can be adapted to desired molding sequences. For example, in reaction injection molding (RIM) processes, the polymerization reaction should start almost immediately with concurrent crystallization and be completed in less than a few minutes so that molded parts can be removed and the molding operation repeated without thermal cycling. For this application, an extremely fast catalyst is desired. On the other hand, in resin transfer molding (RTM), a relatively long induction time (a few minutes) is required for the slow transfer of the liquid c-PBT oligomers to the mold prior to the induction of rapid polymerization. For this purpose, a fast catalyst with a high induction time is necessary. Polymerization of c-PBT oligomers, using tin and titanium catalysts, has been extensively investigated by General Electric and Cyclics Corporation.[11−15] In this regard, a mere 0.25 wt% of stannoxane catalyst (I) has been found capable of completing c-PBT polymerization within 2−3 min at 190 °C; it is considered a fast catalyst. Similarly, a small amount (~0.3 wt%) of catalyst such as butyltin chloride dihydroxide (II) or tetrakis-(2-ethylhexyl) titanate (III) can drive the c-PBT polymerization to completion within 3−5 min at 190 °C while allowing more than 15 min induction time in the tetrakis-(2-ethylhexyl) titanate system, which is an example of fast catalyst with high induction time. Despite these advantages and the availability of catalytic systems for c-PBT oligomers, the polymers thus obtained are not necessarily satisfactory. Rapid concurrent crystallization during polymerization often results in crystallinity that is too high, which decreases certain properties, such as ductility.[16,17] Therefore, it is of interest to understand the effect of these catalysts on the crystallization behavior at different polymerization temperatures and to control related properties of the resulting c-PBT polyesters while retaining the advantages of c-PBT oligomers as precursors for composites.

The present work seeks to understand the effect of catalysts and of polymerization temperatures on the polymerization, polymer conversion, and competing crystallization effects. For that purpose, we performed time-resolved small-angle light scattering (SALS) as a measure of crystallization kinetics of the c-PBT polymers using different catalysts. Gel permeation chromatography (GPC) was used to find conditions for the highest possible conversion and highest molecular weight. WAXD experiments provided further understanding of crystallinity and the crystal lattice parameters of the resulting polyesters.

2. Experimental Section

Materials. Cyclic oligomers of poly(butylene terephthalate) of molecular weight $M_w = (220)n$ [with $n = 2-7$] and catalysts stannoxane (XB2) (I), butyltin chloride dihydroxide (XB3) (II), or tetrakis-(2-ethylhexyl) titanate TyzorOGT (referred to as OGTR) (III) (see Scheme 1) were provided by the Cyclics Corporation.

Preparation of Melt-Mixed c-PBT−Catalyst Systems. The c-PBT oligomers and catalysts used in this study were supplied premixed by the Cyclics Corporation. General procedures for combining c-PBT oligomers and catalyst are described in a US patent assigned to Cyclics Corporation.[18]

Bulk Polymerization of c-PBT Oligomers. Required amounts (~2 g) of previously dried c-PBT oligomers and catalyst (dried at 80 °C for 12 h in a vacuum oven) were placed

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* Author to whom correspondence should be addressed.

[†] Department of Polymer Science & Engineering.

[‡] Department of Chemical Engineering.

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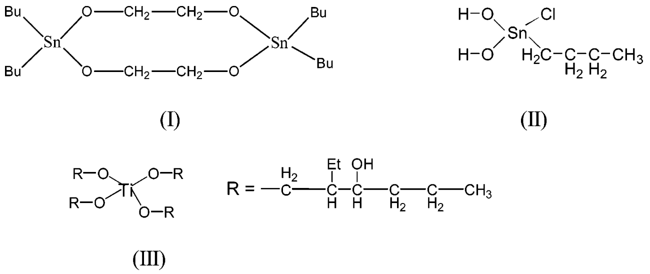
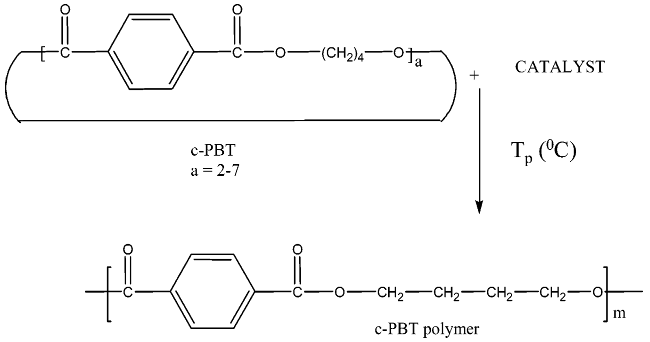
Scheme 1. Various Initiators for the Polymerization of c-PBT Oligomers.



Scheme 2. Catalytic Polymerization of c-PBT Oligomers to c-PBT Polymers



in a vial equipped with a magnetic bar and sealed with Teflon septa. The vial was flushed with dry nitrogen gas for about half an hour, placed in a silicone oil bath, and heated to 160 °C within 8−10 min under constant stirring. Subsequently, the temperature was further raised to the required polymerization temperature (185−205 °C) together with a gentle dry N_2 purge under constant stirring and the polymerization reaction resumed (Scheme 2). Stirring was stopped immediately. After 3 min reaction, the vial, together with its contents, was placed into an ice bath for 4−5 min. The N_2 purge was stopped, and finally, the resulting polymer was vacuum-dried at 80 °C for 12 h. Polymers produced with stannoxane (I), butyltin chloride dihydroxide (II), or tetrakis-(2-ethylhexyl) titanate (III) catalysts are designated arbitrarily as XB2, XB3, and OGTR, respectively.

Small-Angle Light Scattering (SALS). The SALS setup was equipped with a hot-stage (CSS 450 from Linkam Scientific Instruments) for containing the sample. Linearly polarized light from a 10 mW He−Ne laser (wavelength 632.8 nm) passes through a half-wave plate (for rotation of the polarization direction) and then through the sample. Scattered light from the polymer sample is projected onto a polarizing screen and imaged by a CCD camera (Panasonic, WV − BP310). SALS patterns from H_v crossed polarizers and V_v parallel polarizer were recorded, digitized, and analyzed as a function of time during the polymerization reaction. The main beam of the transmitted light passes through a hole in the center of the screen, through a second polarizer, and on to a photodiode for intensity recording. The SALS setup is used for transmittance measurements under the parallel polars to study in-situ polymerization in the hot-stage. For this, a sample of dried, melt-mixed c-PBT/catalyst was placed in the hot-stage. The temperature change in the hot-stage was programmed for the polymerization study as follows. (a) First, it was heated to 150 °C and held there for 10 min to completely melt the oligomer/catalyst, (b) was equilibrated at a chosen polymerization temperature, T_p (185−205 °C or less for XB2 system), and was retained at T_p at least for 100 min until polymerization was complete.

For the crystallization study in the SALS experiment, the polymer is kept in the hot-stage for the following temperature protocol: (a) first heated to 250 °C and kept isothermally for 10 min, (b) equilibrated at various crystallization temperatures, T_c's °C (which are equal to the polymerization temperature), and held for 120 min. Data are recorded immediately after cooling had started.

Table 1. Molecular Weights and Polydispersities of c-PBT Polyesters

catalytic system	T_p (°C)	% yield (polymer)	M_n [g/mol] × 10^4	PDI (M_w/M_n)
XB3	185	65	3.16	2.6
	190	77	3.48	2.6
	195	93	4.66	2.6
	200	94	4.62	2.6
	205	97	5.01	2.6
OGTR	185	84	5.48	2.5
	190	87	5.51	2.4
	195	94	5.77	2.5
	200	95	5.47	2.5
	205	92	5.2	2.6
XB2	175	83	4.5	2.7
	180	84	4.16	2.9
	185	84	4.1	2.9
	190	92	4.18	2.7
	195	94	4.22	2.8

Gel Permeation Chromatography. The number-average molecular weight (M_n), weight-average molecular weight (M_w), and polydispersity index (M_w/M_n) were obtained using gel permeation chromatography (GPC). The GPC was performed on a modular system comprising a Waters 590 HPLC pump, a Waters 717 autosampler, and an ERMA ERC7515A refractive index detector (ERMA CR, Inc., Tokyo). The mobile phase was unstabilized $CHCl_3$ at a flow rate of 0.95 mL/min at 30 °C. The molecular weights were calculated using 13 narrow distribution polystyrene standards from 6 300 000 to 580 g/mol (Pressure Chemical Co., Pittsburgh, PA). The c-PBT polymers were dissolved in a mixture of chlorofom/dichloromethane/1,1,1,3,3,3-hexafluro-2-propanol (60:30:10 v/v/v). Details of the bulk-polymerized c-PBT polyesters are shown in Table 1.

Wide-Angle X-Ray Diffraction (WAXD). Wide-angle X-ray diffraction data were collected on a D500 Siemens diffractometer using Cu K_α (40 kV, 35 mA) radiation and a secondary-beam graphite monochromator. The spectra were recorded in the 2θ range from 2° to 40° in steps of 0.08° and a counting time per step of 1 s. Crystallinity and the d-spacings of the polymers are reported in Table 2.

DSC Study. Differential scanning calorimetry (DSC) was performed on a TA instrument Q_{1000} calibrated with indium. Two sets of experiments were performed in the DSC: (a) experiments with samples of melt-mixed c-PBT/catalyst mixture for the polymerization study and (b) experiments with samples of bulk-polymerized c-PBT polymers. In both cases, samples ranged from 8 to 10 mg and were run under dry nitrogen to prevent moisture and oxidative degradation. Samples underwent the following temperature protocol in the polymerization case: (a) heated to 150 °C and kept isothermally for 10 min, (b) equilibrated at various T_p's (temperature of isothermal polymerization) and held isothermally at 120 min, and (c) heated to 250 °C at a 10 K/min heating rate. For crystallization studies, bulk polymerized samples were run from 30 to 260 °C at a 10 K/min heating rate. The crystallinity of the polymers was calculated according to the following relation and tabulated in Table 3:

$$X_c(\%) = (\Delta H_f/\Delta H^\circ_f)100$$

where ΔH_f is the measured heat of fusion for the sample, and ΔH°_f is the heat of fusion for a 100% crystalline polymer. According to previous studies, the heat of fusion of 100% crystalline PBT is 85.75 J/g.[19]

3. Results and Discussion

3.1. Polymerization. *3.1.1. Transmittance Measurement.* The extent of polymerization of c-PBT oligomers in the presence of different catalysts was studied by monitoring the change in light transmittance intensity at several temperatures of polymerization. It needs to

Table 2. Crystallinity and *d*-Spacing of c-PBT Polymers from WAXD

catalytic system	T_p (°C)	crystallinity (%)	*d*-spacing (Å)						
			d_{001}	d_{010}	d_{002}	d_{200}	d_{011}	d_{100}	d_{101}
XB3	185	64	10.49	5.949	5.624	4.738	4.115	3.885	3.034
	190	64	10.35	5.791	5.542	4.563	4.061	3.822	3.135
	195	65	10.22	5.784	5.536	4.542	4.029	3.812	3.115
	200	66	10.21	5.782	5.512	4.539	4.022	3.804	2.981
	205	68	10.08	5.742	5.370	4.469	3.987	3.698	2.965
OGTR	185	66	10.08	5.823	5.336	4.469	3.970	3.698	2.948
	190	64	10.18	5.949	5.512	4.587	4.115	3.773	3.016
	195	62	10.24	5.964	5.624	4.595	4.178		3.019
	200	62	10.26	5.982	5.605	4.615	4.197	3.789	3.116
	205	60	10.35	5.995	5.711	4.621	4.210		2.999

Table 3. DSC Data of c-PBT Polyesters

catalytic system	T_p (°C)	$T_{m,max}$ (°C) (bulk)	crystallinity (%)
XB3	185	221	55
	190	222	56
	195	226	67
	200	227	66
	205	227	66
OGTR	185	222	63
	190	222	60
	195	223	55
	200	223	52
	205	223	51
XB2	185	228	63
	190	228	64
	195	229	63
	200	229	62
	205	229	60

be mentioned here that between T_g (40 °C) and T_m (235 °C) of the c-PBT polymer, crystallization follows polymerization at any chosen polymerization temperature T_p (165−205 °C).

Figure 1 shows the change in transmittance with time of the XB3 system for polymerization temperatures ranging from 185 to 205 °C. The transmittance value shows 100% at 150 °C because of the complete melting of the c-PBT oligomers. As the temperature reached the appropriate T_p (185−205 °C), the c-PBT oligomers polymerized to c-PBT polymer and started to crystallize as the molecular weight increased. As mentioned above, the T_m of c-PBT polyester is approximately 230 °C and therefore, at any temperature below 230 °C, the c-PBT polymer undergoes crystallization. This results in the loss of light intensity due to scattering from heterogeneous clusters of c-PBT polymer crystal (Figures 1−3). The transmittance starts to decrease after an induction time of nearly 1000 s (~16 min) when the temperature of polymerization is low (below 200 °C). The induction time increases further with increasing temperature of polymerization (Figure 1). The shift in induction time may depend on the degree of undercooling ($T_m - T_c$). When the polymerization temperature is relatively low (185−195 °C), the transmittance cannot decrease to zero, even after a prolonged time interval at constant temperature. On the other hand, at the T_p's of 200 and 205 °C, the c-PBT polyester scatters fully and transmittance decreases to zero with time (Figure 1). These results indicate nearly complete conversion [(maximum decay in transmittance in a particular T_p) × 100] of the c-PBT oligomers to the c-PBT polyesters at 200 and 205 °C, respectively. In comparison, a conversion of nearly 50−60% of c-PBT oligomers to c-PBT polymer is observed when the T_p is below 200 °C. Considering the change in normalized transmittance from 1 to 0 for different temperatures of polymerization (Figure 1), a

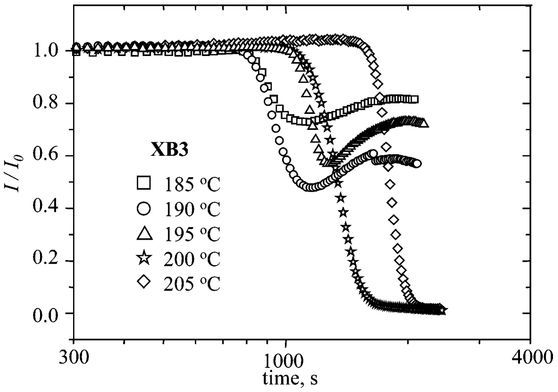


Figure 1. Evolution of light transmittance during the in-situ polymerization of c-PBT oligomers in the presence of the XB3 catalyst system.

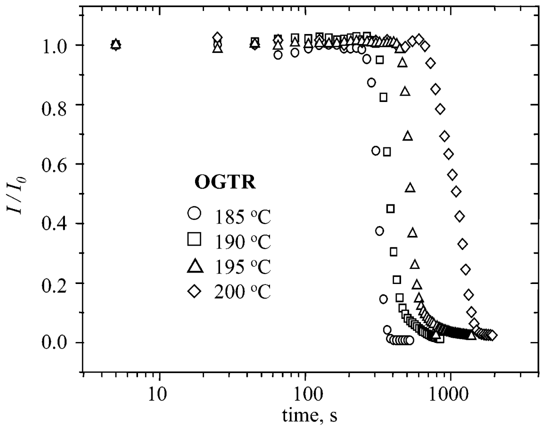


Figure 2. Evolution of light transmittance during the in-situ polymerization of c-PBT oligomers in the presence of the OGTR catalyst system.

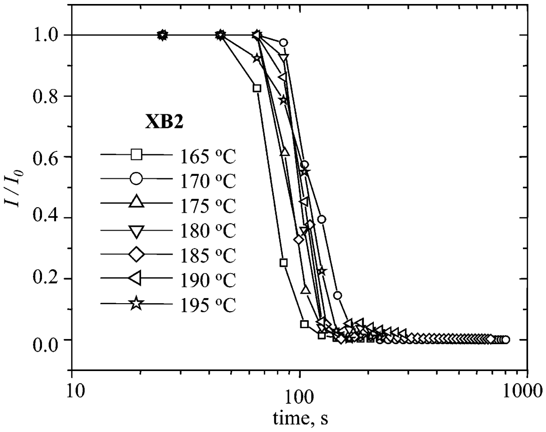


Figure 3. Evolution of light transmittance during the in-situ polymerization of c-PBT oligomers in the presence of the XB2 catalyst system.

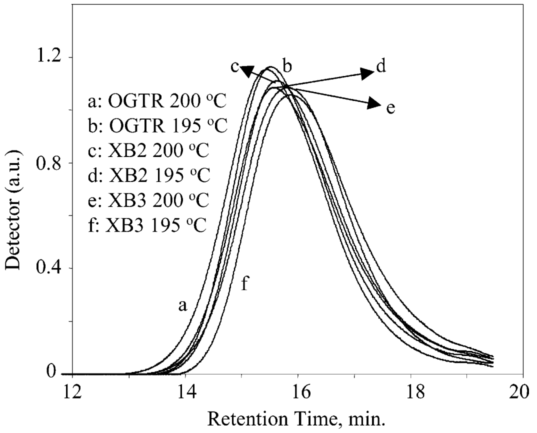


Figure 4. GPC traces for the c-PBT polymers, polymerized at 195 and 200 °C, respectively, using XB3, OGTR, and XB2 catalytic systems.

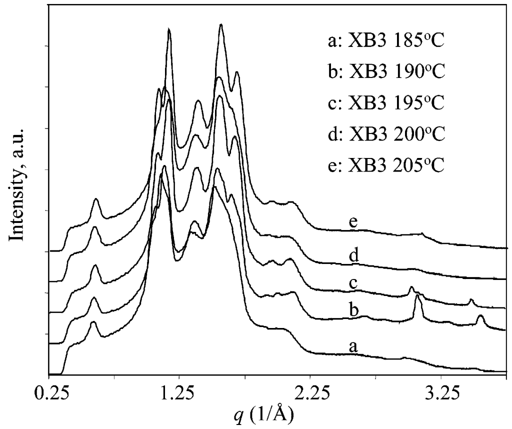


Figure 5. "q" dependence of the intensity in arbitrary units for the WAXD of in-situ polymerized c-PBT polymers in the presence of XB3 catalyst ($q = 4\pi \sin \theta/\lambda$, $d = 2\pi/q$).

steep decrease in the transmittance is observed when polymerization takes place at 200 and 205 °C, respectively, and it requires barely 1.5–2 min to complete the polymerization–crystallization. Further details of the polymerization will be explained in the section on GPC.

Figure 2 shows the change of transmittance over time for the OGTR systems at polymerization temperatures from 185 to 200 °C. The onset of a decrease in the transmittance curves (induction time) increases with temperature of polymerization, as found before with the XB3 system (Figure 1). However, polymerization–crystallization sets in earlier for OGTR than for the XB3 system at any corresponding polymerization temperature. In contrast to the XB3 system, transmittance of the OGTR system decays more steeply and it reaches a zero value regardless of temperature of polymerization. These results suggest a virtually complete conversion of c-PBT oligomers to c-PBT polymers and a similar rate of reaction at all temperatures of polymerization studied.

The fastest polymerization reaction was encountered in the XB2 system, as shown in Figure 3. Although the same trend of the induction time is observed at different temperatures of polymerization (Figures 1 and 2), the difference in induction time is only a few seconds. In contrast to the two previous cases, the XB2 system needs about a minute to resume the crystallization. A steep fall in transmittance curves in the XB2 system also suggests a high rate of polymerization–crystallization. Also the change in normalized transmittance from 1 to 0 suggests a high percentage conversion of c-PBT oligomers to c-PBT polymers in the XB2 catalytic systems.

3.1.2. Gel Permeation Chromatography. The GPC traces for bulk-polymerized c-PBT oligomers in the presence of catalysts at various polymerization temperatures, shown in Figure 4, exhibit a single peak, which differs in magnitude and elution volume between samples. The polymerization performed at higher temperature in a particular catalytic system gives a lower elution volume, suggesting higher-molecular-weight polyester than that of lower polymerization temperature (Table 1). Polymer produced using the OGTR system gives the highest molecular weight. Polyesters obtained using XB3 and XB2 catalysts have the lowest and the intermediate molecular weights, respectively (Table 1, Figure 4). A low-molecular-weight tail is not observed in the higher temperature of polymerization in any of the GPC traces, and the polymer yield reaches more than 95% in most of the catalytic systems when polymerizing at a relatively higher temperature (Table 1). The number-average molecular weight varies from 30 000 to 50 000 g/mol in the XB3 system, and the polydispersity index remains almost the same at 2.6 for all polymerization temperatures. As the temperature of polymerization increases, the conversion of c-PBT oligomers to c-PBT polymers varies from 65% at 185 °C to 97% at 205 °C along with an increase in molecular weight. This observation correlates well with the transmittance measurements (Figure 1). The percentage yield in the OGTR and XB2 systems does not change significantly with the polymerization temperature, which is already expressed in the transmittance data (Figures 2 and 3). The number-average molecular weight and the polydispersity index in the OGTR system are nearly the same at all temperatures of polymerization. Polyesters produced using XB2 catalyst also show nearly the same molecular weight but a slightly higher polydispersity index (~2.7–2.9) as compared to the other two catalytic systems (Table 1). The high PDI and relatively low molecular weight in the XB2 catalytic system are observed even at high temperature of polymerization in comparison with the two other catalytic systems, probably because of the very fast reaction rate. The highest-molecular-weight polyester is obtained in the OGTR system at a temperature range from 190 to 200 °C. However, the highest conversion is noticed in the XB3 catalytic system when the temperature of polymerization is more than 200 °C.

Of the three catalytic systems, XB2 is a very rapid system without any induction time. Both XB3 and OGTR are fast catalysts with at least a 15 min induction time. High yields are obtained in both XB2 and OGTR catalytic systems regardless of the temperature of polymerization. This work suggests that it is possible to design a suitable catalyst for c-PBT polymerization with and without an induction time.

3.2. Crystallization. *3.2.1. Wide-Angle X-Ray Diffraction.* WAXD, performed at room temperature on the cooled polyesters, is shown in Figures 5 and 6 for the XB3 and OGTR systems, respectively. The crystal structure of c-PBT polymers is that of the triclinic PBT crystal,[20] with lattice constants $a = 4.83$ Å, $b = 5.94$ Å, $c = 11.59$ Å, $\alpha = 99.7°$, $\beta = 115.2°$, and $\gamma = 110.8°$. It gives rise to the principal crystallographic planes (011), (010), (002), (200), (011), (100), and (101). The normal-

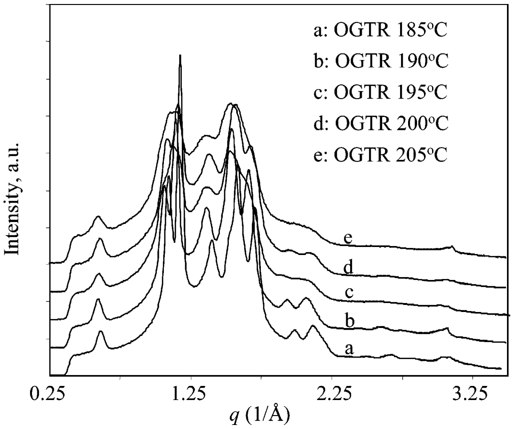


Figure 6. "q" dependence of the intensity in arbitrary units for the WAXD of in-situ polymerized c-PBT polymers in the presence of OGTR catalyst ($q = 4\pi \sin \theta/\lambda$, $d = 2\pi/q$).

ized intensity of the most-prominent peaks corresponding to (200) and (011) planes in the c-PBT polymers varies in both XB3 and OGTR systems. A decrease in d-spacing is observed between 185 and 205 °C polymerization temperature in the XB3 system. This can be explained by an increase in crystal size or formation of a crystal structure with fewer defects.[21] Further, an increase in melting temperature for the polyesters, polymerized at relatively high temperature, occurs (Table 3). A sharp peak (Figure 5) and a high degree of crystallinity (calculated from WAXD, Table 2) at higher polymerization temperature suggest a greater degree of ordering in the XB3 system. However, the intensity of the most-prominent peaks corresponding to the (200) and (011) planes for the OGTR system broadened gradually with increasing polymerization temperature (Figure 6) together with an increase in d-spacing (Table 2). Generally, broadening of the peaks occurs due to the crystal size or defects, as already mentioned. It is worth mentioning here that the molecular weight in the OGTR system remains almost unaffected by the polymerization temperature. However, in the presence of low-molecular-weight unreacted oligomers (see Table 1), the crystallization of the produced polymer could be facilitated to achieve a more defect-free and ordered structure[22] at low polymerization temperature. The same characteristic features, the broad WAXD profile and the low crystallinity, with the increase in polymerization temperature are noted in the XB2 system. It appears that molecular weight and polymerization temperature (rather than type of catalyst) have the most-predominant effect on the crystalline behavior of c-PBT polyesters.

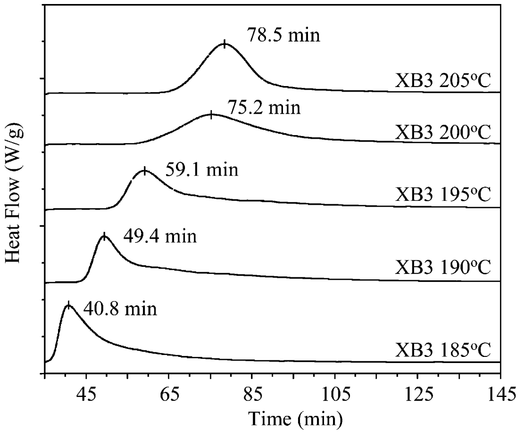


Figure 7. DSC thermograms for the in-situ polymerized c-PBT polymers in the presence of XB3 catalyst.

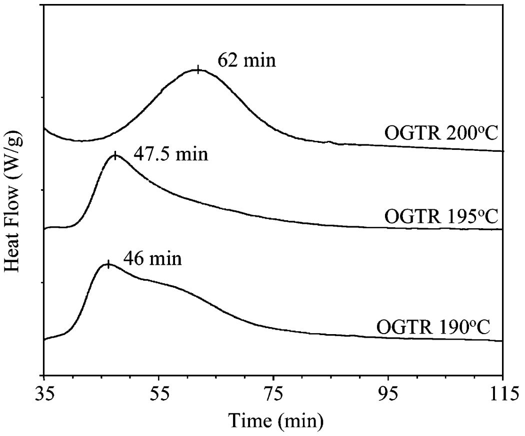


Figure 8. DSC thermograms for the in-situ polymerized c-PBT polymers in the presence of OGTR catalyst.

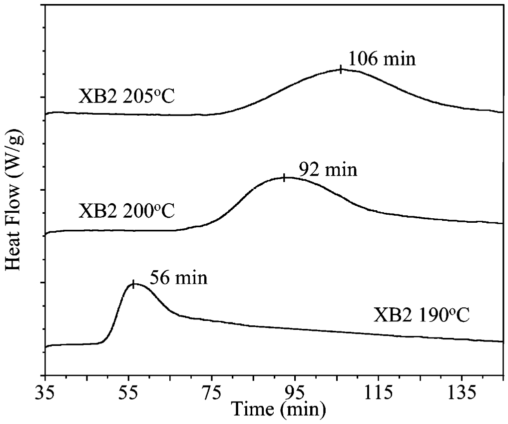


Figure 9. DSC thermograms for the in-situ polymerized c-PBT polymers in the presence of XB2 catalyst.

3.2.2. Differential Scanning Calorimetry. Figures 7−9 show the DSC thermograms of the in-situ polymerized c-PBT oligomers in the presence of different catalytic systems. As for the temperature protocol adopted in the DSC, the blended c-PBT oligomers/catalyst mixture is melted at 150 °C and subsequently heated to a selected T_p where the c-PBT oligomers polymerize inside the DSC pan. Once the polymer is formed at a particular T_p (always lower than the T_m of the c-PBT polymer), it crystallizes. According to the literature,[6,9] the polymerization of cyclic oligomers is entropically driven and the heat evolution due to polymerization is expected to be virtually zero. Therefore, exotherms observed in the DSC thermograms are assigned to the heat change due to crystallization. As expected, the peak position of the crystallization exotherm shifts to longer times because the higher the polymerization temperature, the lower is the degree of undercooling ($T_m - T_c$). Crystallinity calculated from the heat of fusion of the bulk polymerized samples in all cases (Table 3) shows a similar trend to WAXD for all catalytic systems except in the numerical values. The melting point of the polyesters in OGTR and XB2 systems remained almost constant with increasing polymerization temperature (Table 3). However, a large increase in melting temperature of the XB3 system is observed with increasing polymerization temperature due to the molecular-weight increase (see Table 1).

3.3. Crystallization Kinetics. The rapid change of optical properties at an early stage of development of

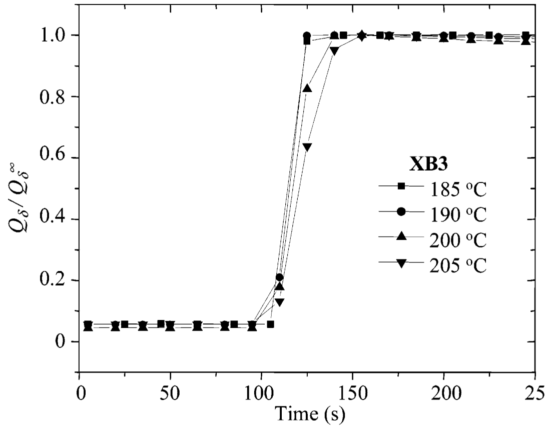


Figure 10. Time evolution of reduced orientation fluctuation invariant during the melt crystallization of XB3-catalyzed c-PBT polymers.

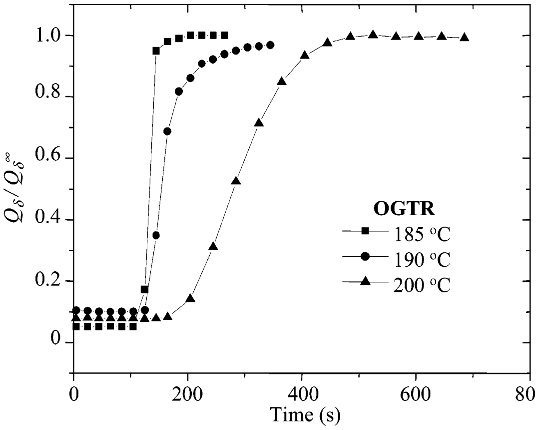


Figure 11. Time evolution of reduced orientation fluctuation invariant during the melt crystallization of OGTR-catalyzed c-PBT polymers.

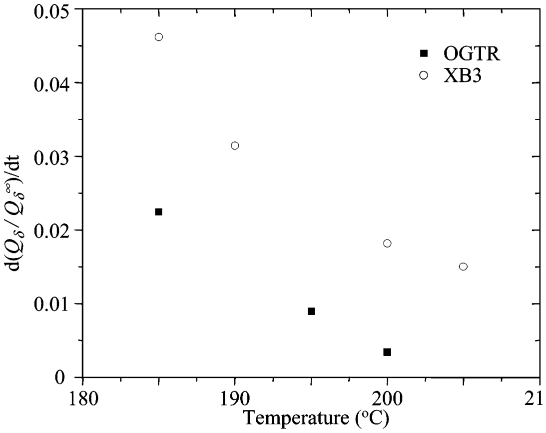
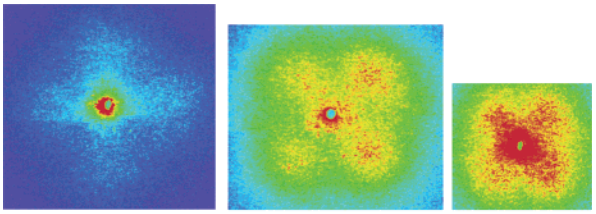


Figure 12. Reduced orientation fluctuation invariant slopes versus crystallization temperature for both XB3- and OGTR-catalyzed c-PBT polymers, respectively.



190°C, 145s

195°C, 190s
$R_s = 4.6$ μm

200°C, 365s
$R_s = 7.5$ μm

Figure 13. Four-leaf-clover patterns for OGTR-catalyzed c-PBT polymers at increasing crystallization temperatures.

crystal structures in the c-PBT polymer makes SALS a suitable technique to study the crystallization kinetics.[23] This method has been applied to observe the spherulitic structure formation at an early stage of crystallization where the structure is of the order of micrometers in size.[24-26] The overall crystallization rate and kinetics can be conveniently described by the integrated scattering intensity or by invariants.[23-24,27-29] Q_δ and Q_η are defined by

$$Q_\delta = \int I_{H_V} q^2 \, dq \qquad \text{(IV)}$$

$$Q_\eta = \int \left(I_{V_V} - \frac{4}{3} I_{H_V} \right) q^2 \, dq \qquad \text{(V)}$$

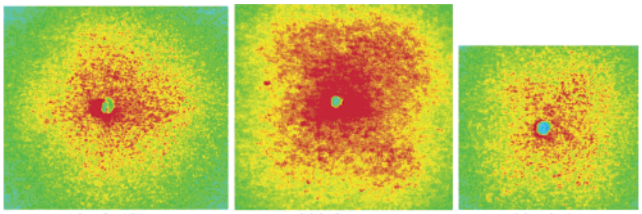
where $q = (4\pi/\lambda) \sin(\theta/2)$ is the scattering vector and I_{V_v} and I_{H_v} are the polarized and depolarized scattering intensity, respectively. In the H_v mode, the invariant Q_δ can be described by the mean square optical anisotropy $\langle \delta^2 \rangle$

$$Q_\delta \propto \langle \delta^2 \rangle \propto \phi_s (\alpha_r - \alpha_t)^2 \qquad \text{(VI)}$$

where ϕ_s is the volume fraction of spherulites, and α_r and α_t are the radial and tangential polarizabilities of spherulites, respectively. A plot of reduced invariant $Q_\delta / Q_\delta^\infty$ versus time, t, where Q_δ^∞ is the Q_δ after a long time of crystallization (up to full solidification of the supercooled melt) can be utilized to find the t_0 (minimum time to resume crystallization) and the crystal fraction at any chosen time. The overall crystallization rate is expressed as the slope $d(Q_\delta / Q_\delta^\infty)/dt$ in the crystallization region.

Figure 10 shows the time variation of the normalized invariant $Q_\delta / Q_\delta^\infty$ of the XB3 catalytically polymerized c-PBT polymer as a function of crystallization temperature from the melt. The $Q_\delta / Q_\delta^\infty$ increases faster at low crystallization temperatures. Similar results are observed in the OGTR systems (Figure 11). At a high temperature of crystallization, Q_δ^∞ increases so that the slope (Figures 10 and 11), which can be regarded as the crystallization rate, decreases. From the inverse slope $[d(Q_\delta / Q_\delta^\infty)/dt]$ of the above curves, we can estimate a characteristic crystallization time (see Figure 12). As expected, the overall crystallization rate decreases with increasing temperature in all cases. It is clear from Figure 12 that the XB3-catalyzed c-PBT polyester crystallizes faster than that of the OGTR-catalyzed c-PBT. This is expected since the degree of undercooling $(T_m - T_c)$ at any particular crystallization temperature is higher for the XB3 system than that of the OGTR (see Table 3). The observed value of t_0 at $T_c = 200$ °C (especially when the polymer yield is sufficiently high) for the OGTR system is 100 s and that of the XB3 system is 130 s.

3.4. Spherulitic Texture. Figures 13 and 14 show the H_v LS patterns after the isothermal crystallization at various crystallization temperatures of OGTR- and XB3-catalyzed c-PBT polyesters from their melt states. A four-leaf-clover-type pattern is clearly observed in the H_v mode in all cases after isothermal crystallization. Time for the appearance of optimum four-leaf-clover increases as the crystallization temperature increases in both cases. When the crystallization temperature is relatively low, the "unusual" type of spherulite is observed in both the XB3 and OGTR catalytic systems;



185ºC, 125s

200ºC, 155s $R_s = 5.1$ μm

205ºC, 345s $R_s = 7.7$ μm

Figure 14. Four-leaf-clover patterns for XB3-catalyzed c-PBT polymers at increasing crystallization temperatures.

however, the “usual” type of spherulite occurs at higher crystallization temperatures (see Figures 13 and 14). These phenomena have been previously reported in other polymeric systems.[9,24,30,31] Spherulites at $T_c = 190$ °C for the OGTR system and at $T_c = 185$ °C for the XB3 system are of the “unusual” type. The one-dimensional H_v scattering profiles at an azimuthal angle of 45° in the scattering patterns of Figures 13 and 14 has a maximum at scattering angle θ_{LS}. The θ_{LS} is related to the average radius of the spherulites, R_s,[32,33] by

$$4.09 = 4\pi(R_s/\lambda_{LS})\sin(\theta_{LS}/2) \qquad \text{(VI)}$$

where, λ_{LS} is the wavelength of the light used. Hence, θ_{LS} is expected to be smaller when R_s becomes larger. The R_s calculated using eq VI from a maximum scattering angle increases with crystallization temperature. R_s for optimally grown ‘usual type’ four-leaf clover spherulites for the OGTR system are shown in Figure 14. The R_s values are calculated as 4.6 μm at $T_c = 195$ °C and 7.5 μm at $T_c = 200$ °C respectively and those for the XB3 system are 5.1 μm at $T_c = 200$ °C and 7.7 μm at $T_c = 205$ °C. As expected, the higher the crystallization temperature, the larger is the spherulite size.

4. Conclusions

This paper describes the suitability of various initiators during the in-situ polymerization of c-PBT oligomers at different polymerization temperatures for reaction injection molding (RIM) and resin transfer molding (RTM) processes. XB2 catalyst completes the in-situ polymerization within 2−3 min, necessary for RIM, at polymerization temperatures of 165 °C and higher. On the other hand, about 15 min of induction time is obtained using initiators such as OGTR and XB3, desired for RTM.

OGTR initiator gives the highest-molecular-weight polymers among all initiators used, and the molecular weight remains the same irrespective of polymerization temperature. However, the molecular weight using XB3 initiators is about 90% of that of the OGTR system when the polymerization temperature is higher than 200 °C. XB2-catalyzed systems give the same molecular weight at all polymerization temperatures and are around 75% of that of the OGTR-catalyzed polymer.

All c-PBT polymers crystallize in the crystallographic lattice of PBT, as confirmed from WAXD. Crystallinity increases with increasing polymerization temperature in the XB3 system, but a reverse trend is noticed both in XB2- and OGTR-catalyzed systems.

The XB3-catalyzed c-PBT polyester crystallizes faster than the OGTR. Crystallization of c-PBT polymers at relatively low temperature results in ‘unusual type’ spherulites, but a ‘usual type’ is observed at higher crystallization temperature both in XB3- and OGTR-catalyzed c-PBT polymers.

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