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Cyclic Oligoesters as Potential Materials for Polymer Nanocomposite Production

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Abstract—Publications dedicated to cyclic oligoesters based on cyclic butylene terephthalate were analyzed and summarized. The features of their preparation and structure and their properties were considered with a special focus on advantages and disadvantages of the methods of their preparation: polycondensation at high dilution and depolymerization. The prospects of application of cyclic butylene terephthalate for polymer nanocomposite production were demonstrated. A development strategy for this research area was suggested.

Keywords: nanocomposites, oligomers, cyclic butylene terephthalate, in situ polymerization, ring-opening polymerization

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INTRODUCTION

One of the main tasks faced today by macromolecular and organic chemistry is the search for new plasticizers suitable as heat-resistant polymer matrices and effective nanoparticles carriers for providing uniform distribution of nanoparticles in various polymer matrices.

Cyclic oligoesters possess a unique combination of rheological and thermal properties making them attractive as matrices for the production of new plasticizers and modifiers of heat-resistant matrices. As of today, however, these are difficultly available compounds, with only cyclic butylene terephthalate oligomer being produced commercially (Cyclics Corporation).

Structure and Properties of Cyclic Butylene Terephthalate Oligomers

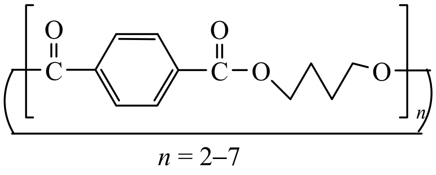
Cyclic butylene terephthalate oligomers are cycles built up of butylene terephthalate units, which consist of residues of butanediol and terephthalic acid (Fig. 1).

Such materials melt in the 120–170°C range and have a very low melt viscosity (15–20 P). Upon adding a catalyst and heating these oligomers undergo ring-opening polymerization which yields a high-molecular-weight polybutylene terephthalate. The properties of the resulting material are similar to those of conventional polybutylene terephthalate. However, the starting materials for its production are low-viscosity oligomers, whereby the resulting product combines the valuable properties of thermosets and thermoplastics.

Due to high heat resistance, favorably coupled with low melt viscosity, resistance to solvents, and good compatibility with polymers, cyclic oligoesters have high potential for use as plasticizers and modifiers of heat-resistant polymers.

Synthesis and Polymerization of Cyclic Oligomers

The main barrier to practical application of cyclic oligoesters is the lack of readily available methods for their synthesis.



$n = 2–7$

Fig. 1. Structure of cyclic butylene terephthalate oligomer.

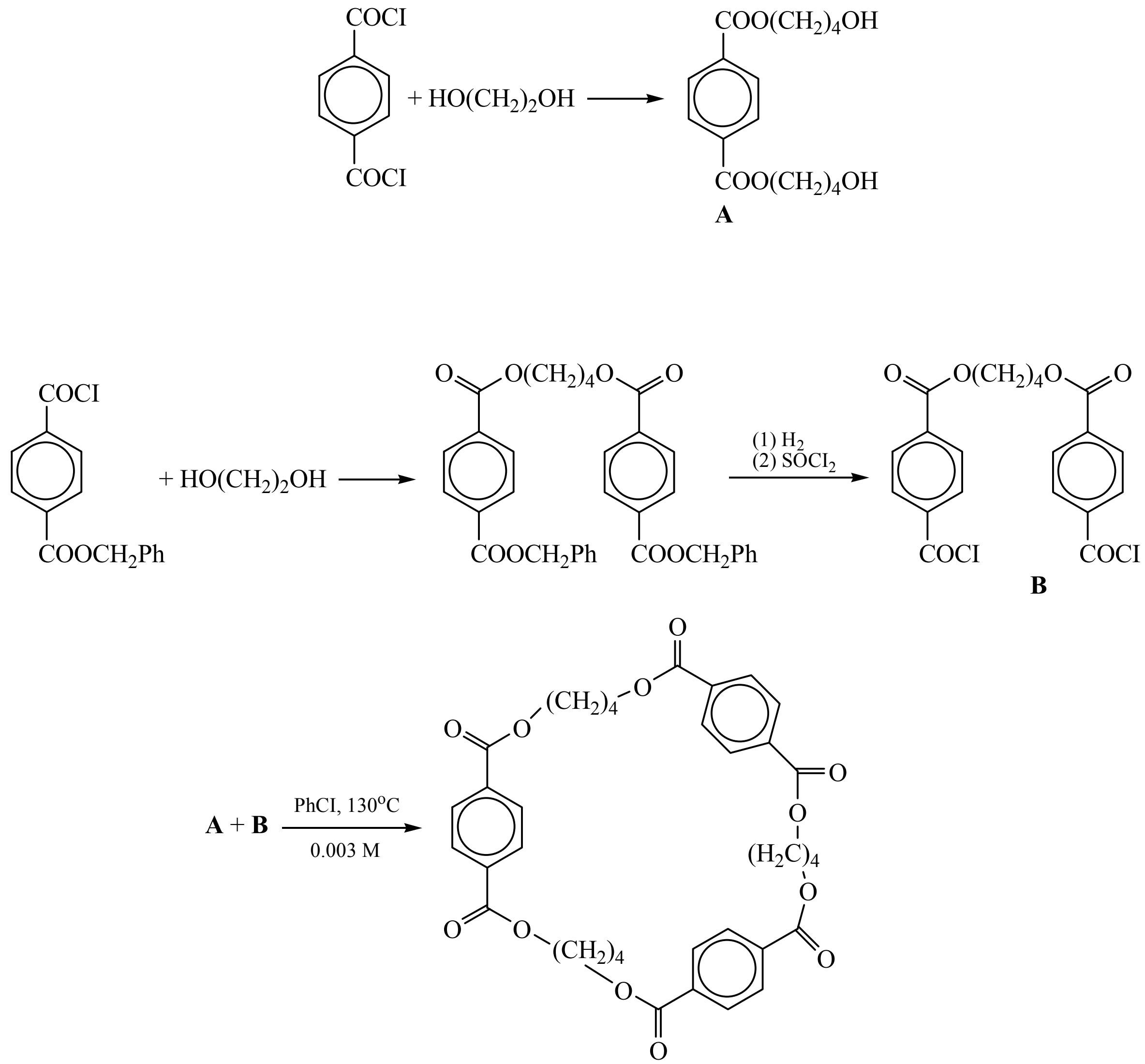


Fig. 2. Synthesis of cyclic butylene terephthalate by direct polycondensation reaction.

This is because, until recently, oligomers have been regarded exclusively as starting materials for polymer production. For this reason the processes of their formation as individual compounds, as well as their chemical transformations and properties are understood now only to a negligible extent.

Cyclic oligomeric esters were first synthesized by a depolymerization reaction in the early works of Carothers et al. [1, 2].

Prior to the 1990s, cyclic oligomeric esters were of academic interest solely. Only since 1995, after butylene terephthalate cyclic oligomer was prepared by depolymerization of commercial polybutylene terephthalate [3], cyclic oligoesters have attracted practical interest.

Cyclic oligomers hold promise as starting materials in the production of macrocyclic systems and as modifiers and plasticizers in the production of new polymers, as confirmed by a number of publications in journals with high impact factors [4–7].

Currently, an active search for synthesis routes to cyclic oligoesters is underway worldwide. The presently known methods for their preparation are polycondensation under high-dilution conditions and depolymerization [8] (Figs. 2 and 3).

However, Brunelle et al. [9] showed that the method of synthesis from highly dilute solutions is not so well suited for the preparation of cyclic oligoesters. They revealed very slow proceeding of the reaction of terephthaloyl chloride with diols, e.g., 1,4-butanediol.

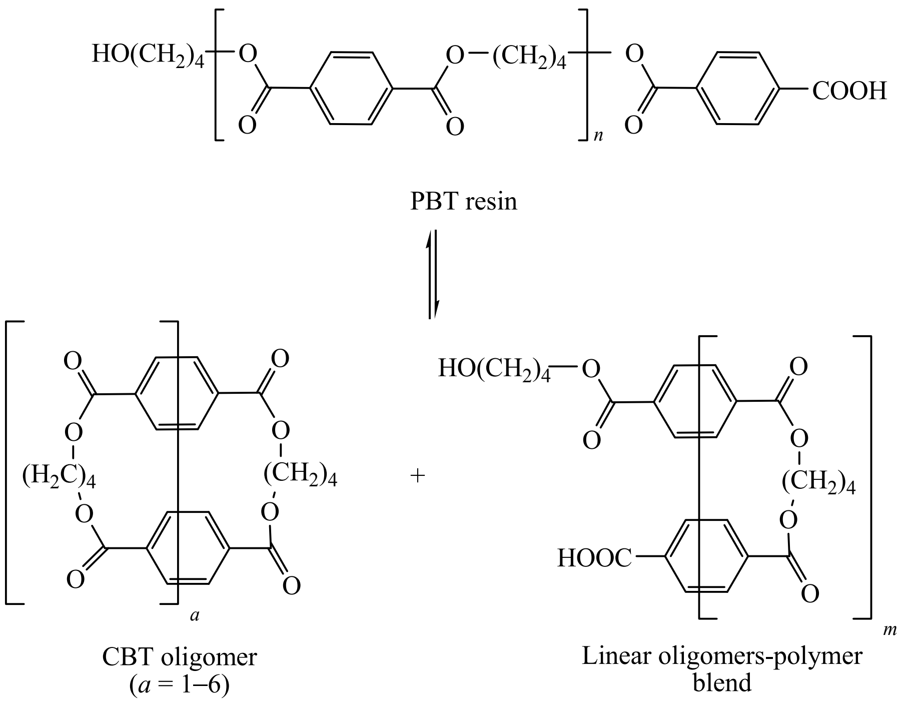


Fig. 3. Synthesis of cyclic butylene terephthalate by depolymerization reaction.

Formation of cyclic oligomers was not observed even upon slowly adding equimolar amounts of terephthaloyl chloride to butanediol in the presence of amines (triethylamine, pyridine, or dimethylaminopyridine) under anhydrous conditions. Wick and Zeitler [10] identified the products and compared them with known commercial materials.

Brunelle et al. also identified side reactions that interfere with the synthesis of cyclic oligomers. This mainly concerns the reaction of amines with acid chloride to form acylammonium chloride, followed by elimination of hydrogen chloride and conversion to an amide. Reaction with the solvent (CH_2Cl_2) gave a salt. Further hydrolysis of the acid chloride yielded carboxylate under the catalyst action (Fig. 4).

Efforts on preparation of cyclic oligoesters by depolymerization were also undertaken at the University of York (the United Kingdom) [11]. The depolymerization techniques developed thereby needed much longer reaction times (24–72 h) for the depolymerization of polyethylene terephthalate (PET). Hodge et al. [12] obtained cyclic oligoesters by the reaction of depolymerization of polyethylene naphthalate.

Hamilton et al. [13] synthesized cyclic oligomers from polyethylene terephthalate, polybutylene isophthalate, polybutylene orthophthalate, decamethylene isophthalate, and decamethylene orthophthalate. The combined use of modern analytical methods revealed the formation of sexamers and, in the case of polyethylene terephthalate, of linear impurities along with cyclic products.

Burch et al. [14] proposed new depolymerization techniques for the preparation of cyclic oligoesters whose polymerization leads to the formation of high-molecular-weight products. Of much interest are their data concerning the preparation of cyclic oligomers, free from byproducts, via depolymerization in solvents, e.g., hexadecane, in which PET or its oligomers are insoluble. For example, cyclic oligoesters that they synthesized from PET in hexadecane refluxing at 287°C for 240 min, followed by filtration to remove the polymer, were free of linear impurities. However, this method gave significantly lower (21%) yields of cyclic oligoesters compared to the solution method.

Anderson [15] reported on the preparation of cyclic oligoesters from dicarboxylic acids, or their diesters, and diols using enzymes, but those studies are now only in their initial stage.

In the 1990s, General Electric undertook the development of efficient methods for the preparation of cyclic

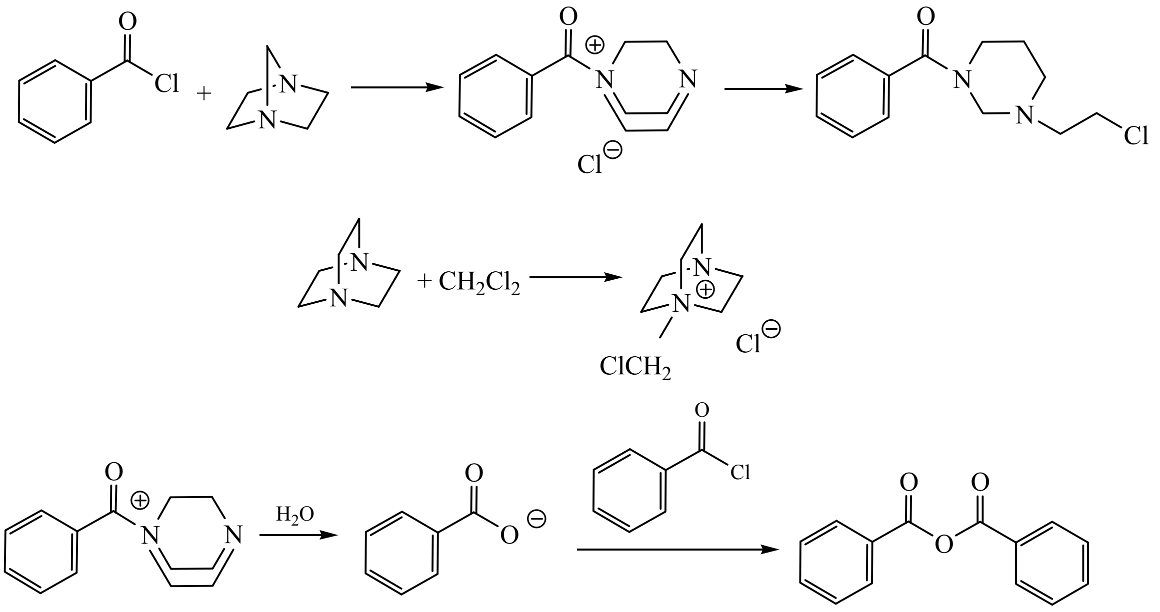


Fig. 4. Side reactions in the formation of cyclic oligoesters.

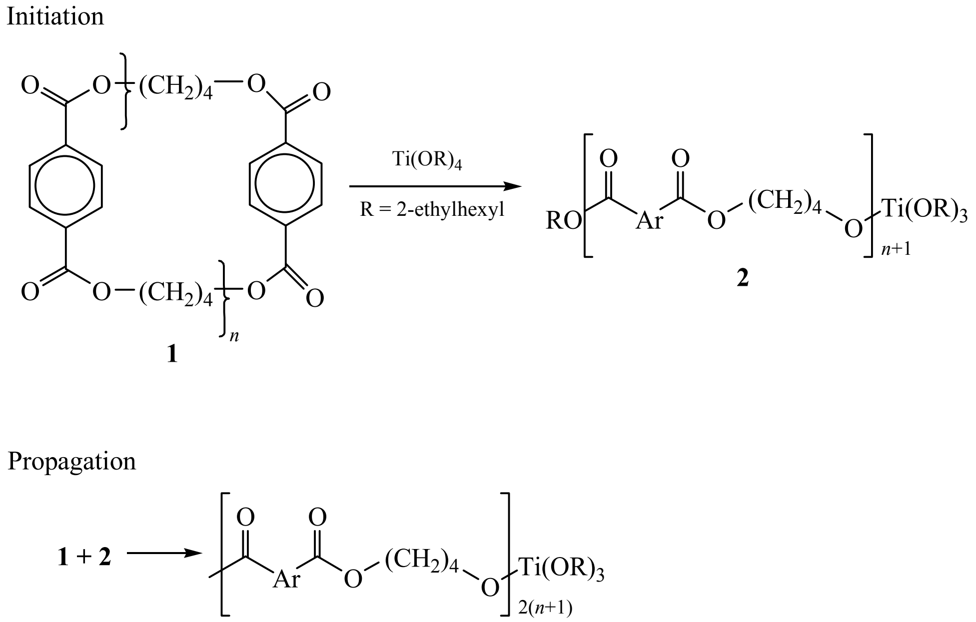


Fig. 5. Reaction of polymerization of cyclic oligoesters.

oligomers of esters using the above-described methods, which efforts were most significantly contributed by Brunelle [16]. This allowed synthesizing a cyclic oligomer of butylene terephthalate with a chain length of up to 6 units by dissolving commercial polybutylene terephthalate in dry *ortho*-dichlorobenzene at reflux in the presence of a catalyst until equilibrium was reached in the cycle formation reaction [3]. The resulting cyclic oligomers underwent ring-opening polymerization into polyesters having unusually long chains [5]. In parallel, a research group led by Semlyen developed a method for the synthesis and polymerization of cyclic ester oligomers and published their results in a series of articles [11, 17–19].

Those studies established a framework for the development of a technology for the preparation of cyclic oligomers of butylene terephthalate, and their production was launched at General Electric in the United States (Schenectady, New York) and in Europe

(Schwarzheide, FRG). This was followed by acquisition of the technology by Cyclics Corporation (FRG). Currently, cyclic butylene terephthalate oligomers are available on the global market under the tradename CBT (abbr. cyclic butylene terephthalate).

Cyclic oligoesters are readily polymerized into high-molecular-weight polyesters in the presence of appropriate catalysts during several minutes at temperatures from 160 to 200°C (Fig. 5) [20, 21].

Out of the modification reactions of cyclic butylene terephthalate, the reactions with ε-caprolactone [22], polycaprolactone [22, 23], and polyvinyl butyral [24] were studied.

Polymer Nanocomposites Based on Cyclic Butylene Terephthalates

As already mentioned, very low melt viscosity of materials based on cyclic butylene terephthalate oligomers makes them suitable for the production of thin-walled complex-shaped items. Figure 6 shows possible conformational states of cyclic oligoesters.

Such materials can also be processed by casting, rotational molding, i.e., by methods that do not require high pressure. Also, due to their high flow, cyclic oligomers are suitable for preparation of high-filled composites.

Cyclic butylene terephthalates offer promise as matrices for polymer nanocomposites. Several studies explored the possibility of using cyclic butylene terephthalate (CBT) oligomer in the preparation of nanocomposites; in particular, graphene-based nanocomposites were prepared [26, 27]. Berti et al. [28] polymerized CBT at 205°C and used montmorillonite (MMT) to prepare nanocomposites; they showed that low melt viscosity of CBT ensured good dispersion of nanoclay.

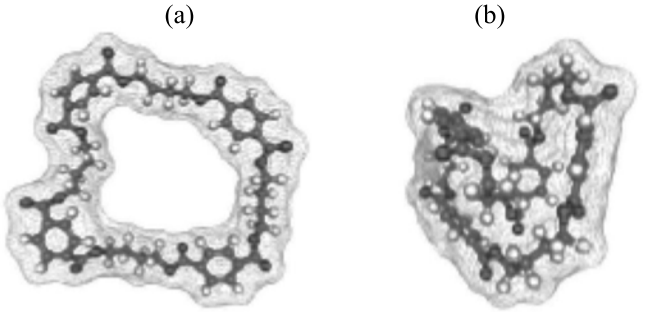


Fig. 6. Conformations of butylene terephthalate cyclic tetramers. (a) $E_{\text{conf}} = 998$ and (b) $E_{\text{conf}} = 950$ kJ/mol [26].

Abt et al. [29] obtained polymer nanocomposites based on poly(methylene diphenyl diisocyanate) (PMDI) with improved physicomechanical properties (Table 1). This is another demonstration of the promise offered by cyclic butylene terephthalate for the production of polymer-layered silicate nanocomposites.

Good dispersion of the nanoparticles in the polymer matrix was demonstrated by means of transmission electron microscopy (Fig. 7).

Nanocomposites based on CBT and on nanoclays were also prepared by Tripathy et al. [30]. To this end

Table 1. Physicomechanical properties of the polymer nanocomposites based on poly(methylene diphenyl diisocyanate) (PMDI)

Composition[a]	Tensile modulus, GPa	Tensile strength, MPa	Elongation at break, %
pCBT(melt)	2.9±0.3	60±2	8±1
pCBT(soln)	3.0±0.2	63±4	9±2
pCBT/PMDI/Cl30B98/1/1(melt)	3.0±0.4	58±1	81±77
pCBT/PMDI/Cl30B98/1/1(solv)	3.7±0.5	62±2	20±15
pCBT/PMDI-p-Cl30B1%(melt)	3.2±0.4	61±3	15±13
pCBT/PMDI-p-Cl30B2%(melt	3.2±0.2	63±2	9±3
pCBT/PMDI-p-Cl30B3%(melt)	3.3±0.2	66±1	7±1
pCBT/PMDI-p-Cl30B1%(solv)	3.0±0.2	58±1	56±21
pCBT/PMDI-p-Cl30B2%(solv)	2.6±0.1	53±1	21±9
pCBT/PMDI-p-Cl30B3%(solv)	2.4±0.2	50±6	4±2
pCBT/PMDI /Cl30B96/1/3(melt.)	3.2±0.2	66±1	16±10

[a] pCBT is polymerized cyclic butylene terephthalate, and Cl30B, Cloisite 30B organoclay (Southern Clay Products, Gonzales, TX, USA).

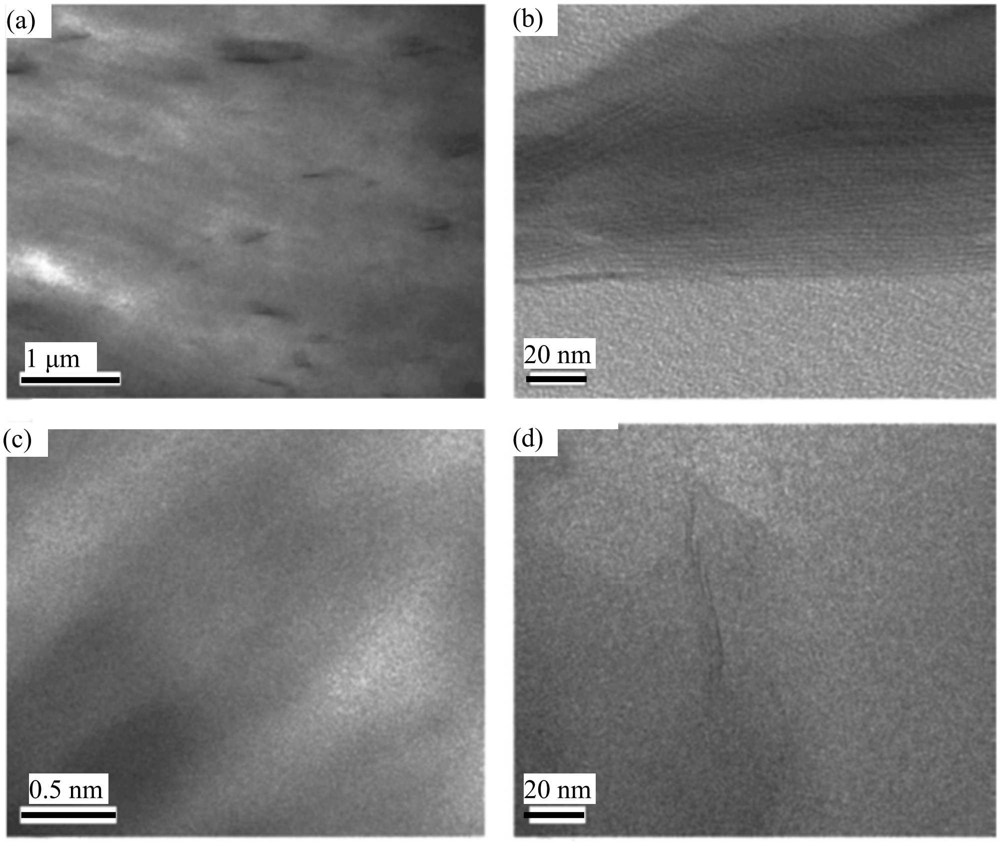


Fig. 7. Microphotographs of the composite materials prepared by the melt blending method: (a, b) pCBT/PMDI/Cl30B98/1/1 and (c, d) pCBT/PMDI-p-Cl30B1%.

they used Cloisite 20A and MMT (both available from Southern Clay Products) and uncatalyzed cyclic butylene terephthalate oligomer. The process involved the preparation of a concentrated masterbatch of the nanoparticles, followed by polymerization at 190°C. A transmission microscopy analysis showed that most of the nanoclay was exfoliated in the nanocomposite. An increased thermal stability, i.e., a 10°C shift in the decomposition onset temperature, was revealed. However, physicomechanical properties of those compositions were not studied.

Liu et al. [31] reported a lower crystallization temperature for composites based on CBT and nanosized Al_2O_3 as compared to conventional polybutylene terephthalate blended with Al_2O_3. Jiang et al. [32] prepared nanocomposites based on CBT and nanosized silica and revealed significant improvement of the mechanical properties of the material.

Study by Wu and Yang [33] was focused on composites based on multi-walled carbon nanotubes (MWCNT) and polybutylene terephthalate. The latter was covalently attached to the MWCNT surface via ring-opening polymerization of CBT oligomer in the presence of a nanofiller containing stannoxane catalyst acting as the immobilized polymerization initiator. The degree of grafting achieved thereby was 59.3%. The solubilities of the functionalized MWCNT in phenol and in tetrachloroethane were determined. Figure 8 shows the reaction scheme.

Bardash [34] examined the interrelations between the preparation conditions and composition, on the one hand, and the viscoelastic, thermophysical, thermal, and electrical properties of nanostructured materials based on CBT and MWCNT, on the other. Table 2 summarizes the results obtained.

Specifically, Table 2 shows how the nanofiller affects the melting temperature (T_m) and the degree of crystallinity (X_{cr}) of the cyclic polybutylene terephthalate (cPBT) matrix. The injection-molded or hot-pressed nanocomposite samples exhibited higher X_{cr} than the extruded strands. This allowed a conclusion that MWCNT acts as nucleators for cPBT and significantly affects the formation of the crystal structure of the cPBT matrix in the nanocomposites [34].

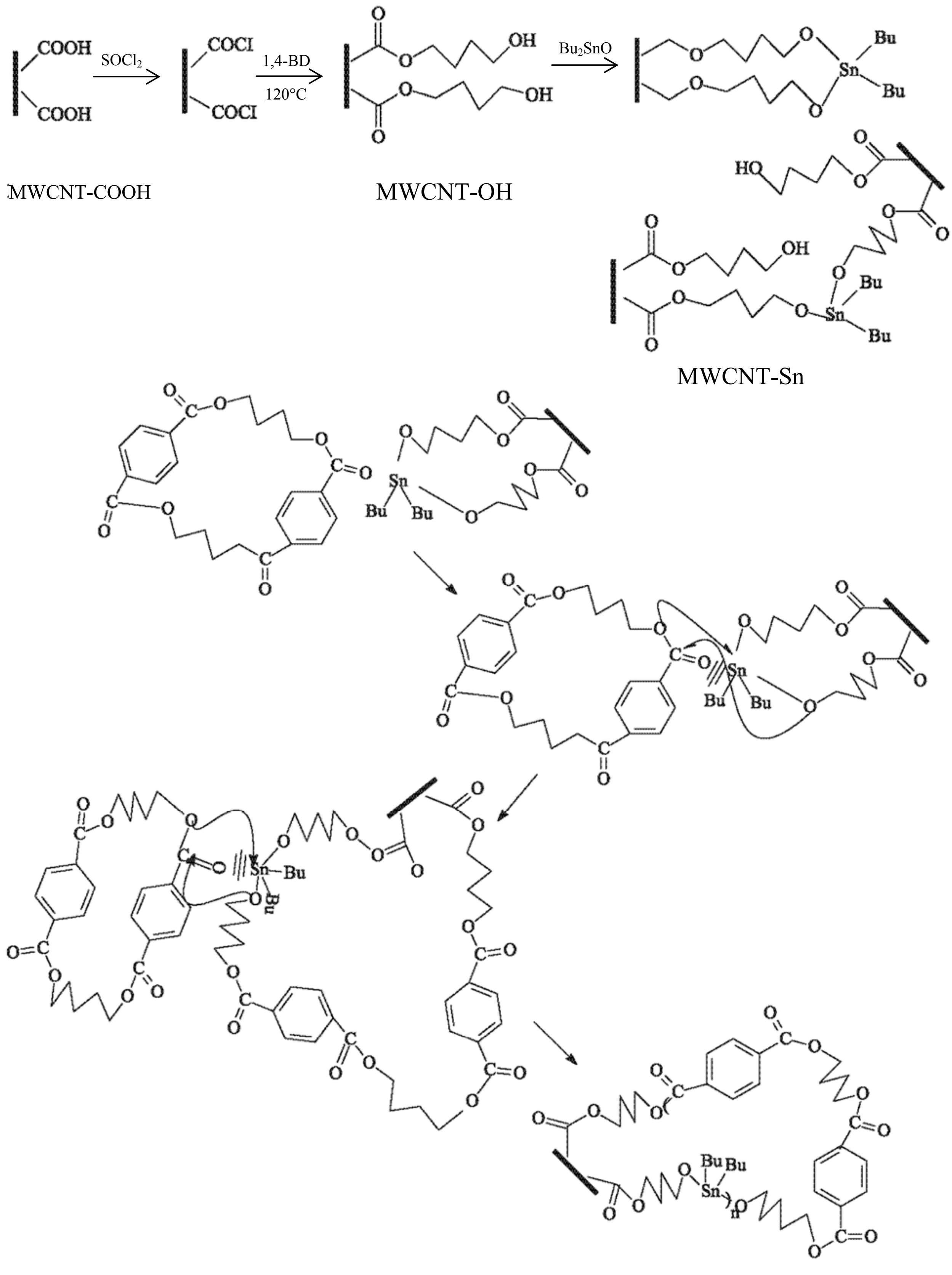


Fig. 8. Schematic of the synthesis of MWCNT-PBT composition.

Table 2. Influence of nanofiller on the melting temperature (T_m) and degree of crystallinity (X_{cr}) of the cyclic polybutylene terephthalate matrix (cPBT-matrix)

MWCNT content, wt %	Injection-molded		Hot-pressed		Extruded strands	
	T_m, K	X_{cr}, %	T_m, K	X_{cr}, %	T_m, K	X_{cr}, %
0.00	495.8	41.0	500.7	38.8	498.1	36.8
0.10	495.5	36.0	502.2	40.0	498.5	29.6
0.30	499.7	39.4	502.1	35.8	499.2	35.0
0.50	498.7	42.6	500.9	40.4	499.1	32.2
1.00	499.2	42.0	501.4	39.8	499.3	33.0
2.00	498.6	47.9	501.7	40.6	498.6	34.9

Table 3. DSC data for polyethylene terephthalate and composites thereof[a]

Composition	T_g, °C	T_m, °C	ΔH_m, J/g	$\Delta H_{cr.\ heat}$, J/g	$\Delta H_{cr.\ cool}$, J/g	$T_{cr.\ heat}$, °C	$T_{cr.\ cool}$, °C	X_{cr}, %
PET	65.7	247.4	31.60	–21.7	–35.40	126.4	213.0	7.30
PET+4% CBT (75%) + organoclay (25%)	67.2	250.5	44.80	–28.5	–38.40	129.3	194.1	12.07
PET+1% CBT (75%) + MMT (25%)	68.5	248.4	38.97	–26.5	–38.96	127.0	196.4	9.10
PET+1% CBT (75%) + organoclay (25%)	61.3	248.4	31.80	–22.0	–33.00	123.7	198.3	7.20

[a] The degree of crystallinity of PET and nanocomposites thereof was calculated by the formula: $X_{cr} = (\Delta H_m - \Delta H_{cr})\times 100/\Delta H_{mo}$, where ΔH_m is the melting enthalpy, ΔH_{cr}, crystallization enthalpy, and ΔH_{mo}, melting enthalpy of the 100% crystalline PET (135 J/g).

Currently, no studies on the synthesis of cyclic oligoesters are being undertaken in the Russian Federation. The reason is that, since the early works of Korshak and Vinogradova (1969–1972) on the equilibrium and nonequilibrium polycondensation reactions, no significant basic research work in this field has been carried out.

Domestic literature includes sporadic publications dedicated to polymer nanocomposites based on CBT and layered silicate nanofillers [35, 36]. Superconcentrates of layered silicate nanoparticles, montmorillonite and halloysite, in CBT were developed [35] and used to prepare nanocomposites based on polypropylene and polybutylene terephthalate by melt blending. Cyclic polybutylene terephthalate-based superconcentrates provided better compatibility of the dispersed components with the polymer matrix and allowed preparation of nanocomposites with improved physicomechanical and processing characteristics.

We employed differential scanning calorimetry in our studies of composites based on polyethylene terephthalate and superconcentrates of layered silicate nanoparticles in cyclic butylene terephthalate [36] and revealed the influence of the nanofiller dispersed in CBT on crystallization of PET (Table 3).

At the same time, we noted that an increase in the degree of crystallinity of PET via modification by layered-silicate fillers had no influence on its performance characteristics. For example, blowmolding of bottles from PET preforms occurred at temperatures below the crystallization temperature, and the presence of fine crystalline structures did not affect the manufacturing process and the quality of the bottle blown thereby. A study of the barrier properties of the resulting composites showed that they were less permeable to CO and O_2 gases in comparison with the initial PET.

CONCLUSIONS

Thus, cyclic oligoesters hold much promise for use in various fields, and especially in the preparation of polymer nanocomposites.

By now, cyclic oligoesters based on ethylene terephthalate and butylene terephthalate and some copolymers and composites thereof have been mostly obtained. Nevertheless, the mechanisms of synthesis of cyclic oligoesters have been understudied, and the potential properties of these compounds are not fully understood. Therefore, a viable development strategy for this research area in the 21st century consists of a search for and introduction of new highly efficient methods for the synthesis of cyclic oligoesters and of new linear and cyclic oligoesters and a comprehensive in-depth study of their properties.

Also, there is an urgent practical need in efficient methods for obtaining cyclic oligoesters intended for the preparation of target products with the desired complex of properties.

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