5.1 Introduction

Rigid thermally stable alicyclic diols are potentially useful comonomers for improving the properties of polyesters. Norbornane ring containing diesters and diols are readily available whose potentials in polymers have not been fully exploited. Wilson et al1 prepared polyesters from norbornane condensed diesters and dimethanols. Polyesters of norbornane and norbornane condensed diesters and dimethanols have high glass transition temperature \( (T_g >100^\circ C) \) and exhibit little tendency to crystallize. The synthesis of copolyesters of PET containing 10-30 \% 2,3-norbornane dimethanol have been reported for applications in hollow fibers having good hardness2. Copolyesters synthesized from dimethyl-e,e-1,4-cyclohexane dicarboxylate, dimethyl perhydro-1,4:5,8-dimethano naphthalene-2,3-dicarboxylate and perhydro-1,4:5,8-dimethanonaphthalene-2,3-dimethanol having excellent transparency and \( T_g >100^\circ C \), which are used in optical applications3.

This chapter discusses the synthesis of copolyesters containing norbornane ring in the chain. Norbornane ring containing diol and diester, namely, 2-exo, 3-endo bis(hydroxymethyl) bicyclo [2.2.1] heptane, dimethyl bicyclo[2.2.1]heptane 2-exo,3-endo dicarboxylate and 2-exo, 3-exo-dimethyl bicyclo[2.2.1]heptane-2-end,3-exo-dicarboxylic acid dimethyl ester were synthesized by Diels-Alder reaction. Copolyesters of dimethyl terephthalate and 1,4-butanediol containing 2,3-bis(hydroxymethyl)bicyclo[2.2.1] heptane and dimethyl bicyclo[2.2.1] heptane 2,3-dicarboxylate were synthesized by melt polymerization. The copolyesters were characterized by \(^1\)H and \(^1\)C NMR spectroscopy. The thermal properties were analyzed by DSC and TGA and crystallization behavior by WAXD.

5.2 Experimental

5.2.1 Materials

Dimethyl fumarate, palladium on carbon 5 wt \% and 10 wt \%, 2-butene-1,4-diol, lithium perchlorate, 2,3-dimethyl maleic anhydride, terephthalic acid 1,4-dimethyl terephthalate (DMT) (99+\%), 1,4-butanediol (BD), Titanium(IV) isopropoxide and N-methyl pyrrolidone (NMP) were obtained from Sigma-Aldrich Inc, USA. Dicyclopentadiene was
obtained from Fluka, Switzerland. Thionyl chloride, ethanol, diethyl ether, toluene, hexane, methanol and ethyl acetate were obtained from s.d. fine-chem. Limited, Mumbai.

5.2.2 Reagents and purification
DMT was recrystallized from methanol. BD was distilled and stored over molecular sieves. Terephthaloyl chloride (TPC) was prepared from terephthalic acid (TPA). TPA was refluxed with freshly distilled thionyl chloride and the excess thionyl chloride was distilled out. TPC was recrystallized twice from dry hexane and distilled under vacuum. NMP was stirred overnight over calcium hydride and distilled under vacuum and stored over molecular sieves. 

Diethyl ether was kept overnight over calcium chloride, distilled and was refluxed over sodium. The solvent was distilled prior to use. Methanol was stirred over calcium hydride and distilled prior to use. 2,3-dimethyl maleic anhydride was purified by vacuum sublimation under high vacuum.

Cyclopentadiene was obtained by thermal cracking of dicyclopentadiene. 200 mL of paraffin oil was taken in a 250 mL three neck round bottom flask equipped with magnetic stirring bar, addition funnel, a 40 cm long fractionating column wound with asbestos tape, distillation condenser and a receiver flask cooled in ice. The paraffin oil was heated to 180-200°C and dicyclopentadiene was added dropwise under vigorous stirring. Cyclopentadiene distilled out at 40°C and was collected in a flask cooled in an ice bath and used immediately.

5M lithium-perchlorate in diethyl ether solution was prepared as follows: Commercially available lithium perchlorate was dried under high vacuum at 160°C for 24 h. The anhydrous lithium perchlorate (27g) and diethyl ether (50 mL) were cooled in an ice bath separately under N₂ atmosphere and then ice-cold ether was added to LiClO₄ through syringe. The dissolution was highly exothermic. The solution was used immediately after preparation.

5.2.3 Synthesis of monomers
5.2.3.1 Synthesis of dimethyl bicyclo[2.2.1]heptane 2-exo,3-endo dicarboxylate (dimethyl 2-exo,3-endo norbornane dicarboxylate) (NBDE)
A 100 mL glass ampoule equipped with a magnetic stirring bar was charged with dimethyl fumarate (2) (20 g, 0.139 mol) and freshly distilled cyclopentadiene (1) (12 g, 0.182 mol). The ampoule was immersed in liquid nitrogen in a N₂ atmosphere and
vacuum was applied for 30 min. The ampoule was sealed under vacuum and heated at 170-180°C for 18 h with stirring. The ampoule was cooled to room temperature and broken. The reaction mixture was then hydrogenated using Pd on carbon (5 wt %) in ethanol at 80°C and H₂ pressure of 1000 psi. The reaction mixture was filtered several times to remove the Pd on carbon completely and concentrated to give 31 g of the diester. The diester was purified by vacuum distillation to give 11.43 g (40%) of pure diester (3). b.p. 66°C/0.01 mbar (lit. 114°C/0.3 mm)

GC Retention time - 6.27 min

IR (neat) - 1733 (C=O), 1433, 1297 (C-O), 1185, 1120, 1051 cm⁻¹

¹H NMR (CDCl₃) δ: 1.1-1.6 (6H, m, CH₂ ring protons), 2.4-2.6 (2H, m, CH ring protons)
2.7 (1H, m, bridgehead CH₂), 3.08 (1H, m, bridgehead CH₂), 3.55, 3.57 (6H, d, OCH₃)

¹³C NMR (CDCl₃) δ: 23.92 (CH₂), 28.44(CH₂), 37.74(CH₂), 39.84 (CH), 41.38(CH), 48.29 (CH), 49.06 (CH), 51.27, 51.42 (OCH₃), 173.38, 174.56 (CO)

5.2.3.2 Synthesis of 2-endo, 3-endo bis(hydroxymethyl) bicyclo [2.2.1]heptane (2-endo, 3-endo norbornane dimethanol) (NBDM)

Cyclopentadiene (1) (42.4 g, 0.64 mol), 2-butene-1,4-diol (5) (42.5 g, 0.48 mol) and 30 mL ethanol were charged into a 300 mL stainless steel Parr reactor. The reactor was purged three times with N₂ and pressurized with 100 psi N₂ and heated to 175°C and reaction continued for 10 h. The reactor was cooled to room temperature and 0.9 g of 5% Pd on carbon was added to the reaction mixture. The reactor was purged with H₂ and pressurized to 300 psi H₂ pressure and heated to 170°C. The reaction was continued until H₂ absorption ceased. The reaction mixture was filtered several times to remove Pd on carbon and concentrated. The semisolid material obtained was purified by vacuum distillation to get 16.4 g of NBDM. b.p. 90°C/0.09 mbar. The NBDM was further purified by recrystallization from toluene/hexane mixture. m.p. 55-57°C (lit. 57-60°C)

GC - 4.29 min (isothermal at 250°C/10 min).

Elemental analysis found (Calcd.) - C: 69.94 (69.23) H: 10.59 (10.25)

Mass (m/z) - 156, 138, 120, 109, 91, 79(100)

¹H NMR (CDCl₃) δ: 1.2-1.55 (6H, m, ring CH₂), 2.25 (4H, m, bridgehead CH₂), 3.64(4H, m, CH₂), 3.93 (2H, t, OH)

¹³C NMR (CDCl₃) δ: 22.49 (CH₂), 39.86 (CH₂), 40.50, 42.94 (CH), 61.31 (OCH₂)
5.2.3.3 Synthesis of 2-exo, 3-endo bis(hydroxymethyl) bicyclo[2.2.1] heptane (norbornane dimethanol) (2-exo,3-endo-NBDM)

A three-neck 500 mL round bottom flask equipped with magnetic stirring bar, addition funnel, reflux condenser and a three-way vacuum adapter was flame dried under vacuum. To lithium aluminum hydride (3.4 g, 0.09 mol) in dry THF (180 mL) was added dimethyl bicyclo[2.2.1]heptane 2-exo, 3-endo dicarboxylate (3) (10 g, 0.047 mol) in THF (180 mL) drop wise over 1 hr with vigorous stirring. The reaction mixture was heated under reflux in N₂ atmosphere for 24 h, cooled to room temperature and treated successively with 3.4 mL H₂O, 3.4 mL of 15% NaOH and 10.2 mL of ILO. The precipitate was filtered and the solvent evaporated. The crude yield of 2-exo,3-endo—2,3-bis(hydroxymethyl) bicyclo[2.2.1] heptane (2-exo,3-endo-NBDM) was found to be 11.15 g. The 2-exo,3-endo-NBDM was purified by vacuum distillation to obtain 6.9 g (94 %) of the pure diol. b. p. 100-104°C/ 0.02 mbar.

GC – 5.52 min (150 for 5 min to 250°C at 10°C/min)

Elemental (found) – C: 69.25 (67.28), H: 10.25 (10.72)

Mass- 157, 174, 313 (M⁺)

¹H NMR (CDCl₃) δ: 1.2-1.8 (8H, m, CH₂ and CH ring protons) 2.01, 2.26 (2H, s, bridgehead CH₂), 3.22(2H, t, OCH₂), 3.46 (2H, t, OH)

¹³C NMR (CDCl₃) δ: 22.37, 30.17, 37.45 (CH₂), 38.95, 39.18, 48.9, 50.49(CH), 64.01, 65.74 (OCH₂)

5.2.3.4 Synthesis of 2-exo, 3-exo-dimethyl bicyclo[2.2.1]heptane-2-endo,3-endo-dicarboxylic acid dimethyl ester (DMNBDE)

A two-neck 100 mL round bottom flask equipped with magnetic stirring bar and a vacuum adapter was flame dried under vacuum and 2,3-dimethyl maleic anhydride (7) (3.5 g, 0.028 mol) was added and cooled to 0°C. 50 mL 5M LPDE (lithium perchlorate in diethyl ether) was added with syringe under stirring. Stirring was continued till all the anhydride was completely dissolved. The contents of the flask were cooled to 0°C and freshly distilled cyclopentadiene (10 mL, 0.124 mol) was added slowly. The reaction mixture was allowed to stir for 48 hrs, diluted by the addition of DCM followed by addition of water. The organic and aqueous layers were separated and the organic layer was washed several times with water. The organic layer was dried over anhydrous sodium sulphate and evaporated to give 5.9 g of 2-exo-3-exo-dimethyl bicyclo[2.2.1] hept-2-ene-2-endo,3-endo-dicarboxylic anhydride. The anhydride was further washed...
with cyclohexane to remove unreacted cyclopentadiene to give 4.0 g (75%) of 2-exo-3-
exo-dimethyl bicyclo [2.2.1] hept-2-ene-2-endo-3-endo-dicaboxylic anhydride. The
anhydride was hydrogenated in ethyl acetate using 10 wt % Pd on C at 700 psi H₂
pressure until H₂ absorption ceased. The reaction mixture was filtered to remove the
Pd/C and evaporation of ethyl acetate gave 2.7g (50%) of 2-exo-3-exo-dimethyl bicyclo
[2.2.1] heptane-2-endo-3-endo-dicaboxylic anhydride (DMNBDA) (8). m.p. 198-200°C
(lit₉, 198-200°C)

IR (neat)- 2963 (CH₃), 2888, 1850 (anhydride C=O), 1772 (anhydride C=O), 1246, 1219,
980

GC - 7.68 min (150 for 5 min to 250°C at 10°C/min)

Elemental (found) – C: 68.04 (68.34), H: 7.2 (7.89)
Mass- 195, 167, 149 (M⁺), 130

¹H NMR (CDCl₃) δ: 1.32 (6H, s, OCH₃), 1.4-1.93 (6H, m, ring protons), 2.38 (2H, m,
bridehead CH₂)

¹³C NMR (CDCl₃) δ: 17.82 (CH₃), 25.39, 37.63, 48.59 (CH₂), 56.89 (CH), 175.73 (CO)

DMNBDA (8) (1.5 g, 7 mmol) and 40 mL of dry methanol were taken in a 100 mL round
bottom flask equipped with a magnetic stirring bar and a reflux condenser. Thionyl
chloride (5 mL) was added slowly under cooling through syringe with rapid stirring.
After the addition was complete the reaction mixture was refluxed for 96 hrs. The
reaction mixture was cooled to room temperature and DCM was added and washed with
water, sodium bicarbonate and again water, the organic layer dried over anhydrous
sodium sulphate and evaporated to give a mixture of DMNBDA and DMNBDE (9). The
mixture of anhydride was difficult to separate. The mixture was heated in dilute
bicarbonate solution when the anhydride dissolved and on cooling the ester crystals were
obtained. This was done several times to get pure DMNBDE. The final yield of
DMBNDE is 1.4 g (76 %). m.p. 52-55°C (lit. 57-59°C)

IR (neat) – 2950 (CH₃), 2883, 1733 (C=O ester), 1536, 1438, 1250, 1119 cm⁻¹

GC - 6.45 min (150 for 5 min to 250°C at 10°C/min)

¹H NMR (CDCl₃) δ: 1.29 (1H, m, CH₃), 1.29 (6H, s, ring CH₂), 1.35-1.5 (2H, m, CH),
1.5-1.95 (3H, m), 2.13 (2H, m, bridgehead CH₂), 3.62 (6H, s, OCH₃)

¹³C NMR (CDCl₃) δ: 22.34 (CH₃), 25.03, 35.71, 48.92 (CH₂), 51.09(OCH₃), 55.09 (CH),
175.94 (CO)
5.2.4 Synthesis of polyester and copolyesters containing 2-endo,3-endo-NBDM (6)

5.2.4.1 Synthesis of poly(2,3-norbornane dimethylene terephthalate) (PNBDT) (10)

5.2.4.1.1 Melt condensation

DMT (2.5 g, 0.013 mol), 2-endo,3-endo-2,3-bis(hydroxymethyl) bicyclo[2.2.1]heptane (NBDM) (6) (3.01 g, 0.019 mol) and titanium isopropoxide (0.1 wt % w.r.t DMT) were taken in a two neck round bottom flask equipped with a magnetic stirring bar, N₂ inlet, air condenser and spiral trap to collect distillate. The flask was heated to 170°C under N₂ atmosphere when methanol distilled out. The reaction was continued at 160-180°C for 2 h and further at 220°C for 4 h and the pressure was gradually reduced over 30 min to 0.02 mbar and reaction was continued for 2 h at 240°C. Polymerization reaction did not proceed and the reaction mixture underwent charring.

5.2.4.1.2 Solution polycondensation of terephthaloyl chloride and norbornane dimethanol

2-endo,3-endo--NBDM (6) (2.56 g, 10 mmol) and 5 mL of NMP were taken in a 50 mL two neck round bottom flask equipped with a N₂ inlet and magnetic stirring bar. The reaction flask was kept under a constant stream of N₂ with stirring till the NBDM completely dissolved in NMP. Terephthaloyl chloride (2 g, 10 mmol) was dissolved in 5 mL of NMP and added to the flask. The reaction mixture was stirred at room temperature. When no more heat was generated and the contents began to solidify, the reaction mixture was heated at 180°C for 2 h. The reaction flask was cooled and precipitated in methanol. The polymer was filtered, washed several times with methanol to remove the trapped NMP and dried at 100°C. Yield = 2.6 g (92 %).

\( \eta_{inh} \) (chloroform) - 0.2 dL/g

GPC (CHCl₃) - \( M_n = 6,700 \ M_a = 14, 900 \ (M_a/M_n = 2.2) \)

\( ^1H \) NMR (CDCl₃) \( \delta: 1.52 \ (6H, m), 2.44, 2.53 \ (4H, m), 4.49 \ (4H, m), 8.05 \ (4H, s) \)

5.2.4.1.3 Solid state polymerization

The PNBDT (10) oligomer (0.2 dL/g) was dried in vacuum oven. The oligomer was powdered and suspended in toluene, 0.01 wt % titanium isopropoxide in toluene was added. The toluene was stripped off at reduced pressure. The dried oligomer powder was subjected to solid state polymerization at 150°C for 6 h under reduced pressure (0.02 mbar). There was no change in viscosity after SSP.
5.2.4.2 Synthesis of copolyester from dimethyl terephthalate, 1,4-butanediol and 2-endo, 3-endo norbornane dimethanol

5.2.4.2.1 Melt condensation of DMT, BD and 2-endo, 3-endo norbornane dimethanol

DMT (5.0 g, 0.026 mol), BD (2.06 g, 0.023 mol), (2-endo, 3-endo norbornane dimethanol) (NBDM) (6) (1.14 g, 9 mmol) and DBTO (0.05 wt % w.r.t DMT) were taken in a two neck round bottom flask equipped with a magnetic stirring bar, N₂ inlet, air condenser and spiral trap to collect distillate. The flask was flushed with N₂ and heated to 167°C under a constant stream of N₂ when methanol distillation started. Reaction was continued at 160-200°C for 6 h and at 220°C for 2 h and the pressure was gradually reduced to 0.02 mbar and reaction was continued for 2 h at 230°C. The reaction flask was cooled under vacuum and the polymer was recovered. Yield = 5.4 g (83 %).

\( \eta_{in} \) (chloroform)- 0.16 dL/g

\( ^{1}H \) NMR (CDCl₃) δ: 1.54 (4H, m, ring CH₂), 2.02 (4H, s, CH₂), 2.4-2.7 (6H, m, ring protons), 4.02 (4H, s, OCH₂ of NBDM), 4.5 (4H, s, OCH₂ of BD), 8.12 (8H, d, aromatic)

5.2.4.2.2 Melt condensation of poly(BT-co-NBDT) oligomer, DMT and BD

DMT (2.5g, 0.013 mol), BD (1.87 g, 0.02 mol), PNBDT oligomer (1 g) and titanium isopropoxide (0.1 wt % w.r.t DMT) were taken in a two neck round bottom flask equipped with a magnetic stirring bar, N₂ inlet, air condenser and spiral trap. The flask was purged with N₂ and heated to 190°C and reaction was continued for 7 h. The pressure was gradually reduced to 0.02 mbar and reaction continued at 250-260°C for 3 h. The flask was cooled under vacuum and polymer was recovered. Yield = 3.6 g.

\( \eta_{in} \) (chloroform)- 0.5 dL/g

\( ^{1}H \) NMR (CDCl₃/CF₃COOD) δ: 2.02 (4H, s, CH₂), 4.50 (4H, s, CH₂O) 8.12 (4H, s, aromatic protons)

5.2.4.3 Synthesis of poly(2,3-norbornane dimethylene terephthalate) (PNBDT)

DMT (2.5 g, 0.013 mol), 2-exo, 3-endo bis(hydroxymethyl) bicyclo [2.2.1] heptane (norbornane dimethanol) (NBDM) (4) (2.15 g, 0.014 mol) and titanium isopropoxide (0.1 wt % w.r.t DMT) were taken in a two neck round bottom flask equipped with a magnetic stirring bar, N₂ inlet, air condenser and spiral trap. The flask was heated to 160°C under of N₂ atmosphere when methanol distilled out. The reaction was continued...
at 160-180°C for 3 h and further at 220°C for 4 h and the pressure was gradually reduced over 30 min to 0.02 mbar and reaction was continued for 6 h at 230°C. The reaction flask was cooled under vacuum and the polymer was recovered. Yield = 3.54 g (96%).

\[ \eta_{\text{inh}}(\text{phenol/TCE 60/40 w/w}) = 0.33 \text{ dL/g} \]

GPC (CHCl₃) \( M_n = 18,300, M_w = 32,800 \) \( M_w/M_n = 1.8 \)

\[ ^1\text{H NMR (CDCl}_3\text{)} \delta: 1.1-1.8 \text{ (8H, m, ring protons), 2.27, 2.42 (2H, d, bridgehead), 4.23, 4.43 (4H, m, OCH}_2\text{), 8.10 (4H, s, aromatic)} \]

\[ ^{13}\text{C NMR} \ - 22.15, 29.55, 36.82, 38.33, 39.18 \text{(CH}_2\text{), 43.43, 45.38 (CH), 66.91, 68.51 (OCH}_2\text{), 129.7, 133.82 (aromatic), 166.71, 166.74 \text{(CO)}} \]

### 5.2.4.4 Synthesis of copolyesters containing dimethyl terephthalate, 1,4-butanediol and 2-exo, 3-endo bis(hydroxymethyl) bicyclo [2.2.1] heptane (norbornane dimethanol) (NBDM)

DMT, 1,4-BD, 2-exo, 3-endo bis(hydroxymethyl) bicyclo [2.2.1] heptane (norbornane dimethanol) (NBDM) and titanium isopropoxide (0.1 wt % w.r.t DMT) were taken in a two neck round bottom flask equipped with magnetic stirring bar, \( \text{N}_2 \) inlet, short path vacuum distillation adapter, spiral trap and a vacuum control assembly. A 1:1.15 ratio of DMT to diol was used in all polymerization and BD/NBDM ratio was varied (90/10, 80/20 and 50/50). The reaction was carried out at 160-220°C for 6-8 h. The pressure was gradually reduced to 0.02 mbar over 20 min and reaction continued at 230-250°C for 10-11 h. The flask was cooled under vacuum and polymer was recovered.

### 5.2.5 Synthesis of polyester and copolyesters containing dimethyl 2-exo, 3-endo norbornane dicarboxylate (NBDE)

#### 5.2.5.1 Synthesis of poly (butylene-2,3-norbornane dicarboxylate) (PBNB)

NBDE (3) (2.12 g, 0.01 mol), BD (1.89 g, 0.02 mol) and titanium isopropoxide (0.1 wt % w.r.t NBDE) were taken in a two neck round bottom flask equipped with magnetic stirring bar, \( \text{N}_2 \) gas inlet, air condenser and spiral trap. The reaction mixture was heated at 160-180°C for 3 h when methanol distilled out and the reaction was continued at 210-260°C for 5 h. The pressure was gradually reduced to 0.02 mbar and reaction continued at 260°C for 4 h. The flask was cooled under vacuum. The polymer was found to be rubbery. Yield = 2.1 (92 %) g.

\[ \eta_{\text{inh}}(\text{CHCl}_3) = 0.6 \text{ dL/g} \]
GPC (CHCl₃) - Mₙ = 37,000 Mₘ = 98,800 (Mₙ/Mₘ = 2.6)

¹H NMR (CDCl₃) δ: 4.11 (4H, m, OCH₂), 3.22 (1H, m, CH), 2.82 (1H, m, CH)) 2.64, 2.56 (1H, m, bridgehead), 1.71 (4H, m, CH₂), 1.2-1.65 (6H, m, ring protons)

¹³C NMR (CDCl₃): 24.11, 25.27, 28.78, 37.93, 40.13, 41.75(CH₂), 48.62, 49.29 (CH-CO), 63.88, 64.0 (OCH₂), 173.2, 174.39 (CO)

5.2.5.2 Synthesis of poly (butylene terephthalate-co-butylene-2,3-norbornane dicarboxylate) (P(BT-co-BNB))

DMT, NBDE, BD and titanium isopropoxide (0.1 wt % w.r.t ester) were taken in a two-neck round bottom flask equipped with magnetic stirring bar, N₂ inlet, short path vacuum distillation adapter and a spiral trap. A 1:1.5 ratio of diester to diol was used in all the polymerization reactions and DMT/NBDE ratio was varied (90/10, 80/20, 70/30 and 50/50). The reaction mixture was heated at 160-220°C for 6-8 h under a constant stream of N₂ gas. The pressure was gradually reduced over 1 h to 0.02 mbar, as the excess butanediol distilled out and reaction was continued at 230-250°C for 10-12 h. The flask was cooled under vacuum and polymer was recovered by breaking and cutting into pieces. The viscosity and thermal properties of the copolyesters are given in the results and discussion section.

5.2.6 Synthesis of poly (butylene-2,3-dimethyl-2,3-norbornane dicarboxylate) (DMNBDE) (9) (1.0 g, 4 mmol), BD (0.6 g, 6.6 mmol) and titanium isopropoxide (0.1 wt % w.r.t DMNBDE) were taken in a two-neck round bottom flask equipped with magnetic stirring bar, N₂ gas inlet, air condenser and spiral trap. The reaction mixture was heated at 160-180°C for 3 h and the reaction was continued at 210-260°C for 4 h. The reaction did not proceed. ¹H NMR shows same spectrum as that of DMNBDE.

5.3 Analysis

5.3.1 Monomer Characterization

¹H and ¹³C NMR were recorded in CDCl₃ or DMSO-d₆ on a Bruker AC-200 NMR spectrometer. The IR spectra were recorded as neat or in chloroform on FTIR 16 PC Perkin Elmer spectrophotometer. Elemental analysis was done on CHNS-O, EA1108-Elemental Anlyser, Carlo-Erba Instruments, Italy. Gas chromatography was done using a BP1 Column. The temperature program used was: Oven - 150°C (5 min) to 250°C at 10°C/min, injector - 260°C and detector 270°C.
5.3.2 Polymer characterization

Inherent viscosities were measured at 30°C in an automated Schott Gerate AVS 24 viscometer, using an Ubbelohde suspended level viscometer in phenol/1,1',2,2'-tetrachloroethane (TCE) (60:40 wt/wt) or CHCl₃ at a polymer concentration of 0.5 wt%. Other characterizations are discussed in Chapter 3.

5.4 Results and discussion

5.4.1 Monomer synthesis

Dimethyl bicyclo[2.2.1]heptane 2-exo, 3-endo dicarboxylate (NBDE) (3) was synthesized by Diels Alder reaction. The first step is reaction of cyclopentadiene (1) with dimethyl fumarate (2) and subsequent reduction using palladium-on-carbon as catalyst which leads to the formation of dimethyl bicyclo[2.2.1]heptane2-exo, 3-endo dicarboxylate (3). 2-exo, 3-endo -bis(hydroxymethyl) bicyclo [2.2.1] heptane (4) was synthesized from NBDE by LAH reduction. The synthetic scheme is illustrated in Scheme 5.1 and the 1H and 13C NMR is shown in Figures 5.1 and 5.2.

![Scheme 5.1](image)

Scheme 5.1 Synthesis of dimethyl bicyclo[2.2.1]heptane-2-exo,3-endo-dicarboxylate (NBDE) and 2-exo,3-endo-bis(hydroxymethyl) bicyclo[2.2.1] heptane (2-exo,3-endo-NBDM)
Literature describes a one pot synthesis of 2-endo,3-endo-bis(hydroxymethyl)bicyclo[2,2,1] heptane (6) starting from 2-butene-1,4-diol (5), which is a weak dienophile. Hence the reaction was done under pressure, which lead to the formation of
the endo-endo isomer. The Diels-Alder reaction of cyclopentadiene (1) with cis-2-butene-1,4-diol was done under nitrogen pressure followed by reduction with Pd on C to give the 2-endo,3-endo bis(hydroxymethyl) bicyclo [2.2.1]heptane (6) as given in Scheme 5.2.

Scheme 5.2 Synthesis of 2-endo,3-endo-bis(hydroxymethyl) bicyclo [2.2.1]heptane (2-endo,3-endo-NBDM)

Kreiser et al. synthesized 2-exo,3-exo-dimethyl bicyclo[2.2.1]heptane-2-endo,3-endo-dicarboxylic anhydride (8) by Diels-Alder reaction of cyclopentadiene and dimethyl maleic anhydride (7) at 90°C for 12 h in benzene with a yield of 55%. The anhydride was further hydrolyzed using sodium methoxide-dimethyl sulphate to get 2-exo,3-exo-dimethyl bicyclo[2.2.1]heptane-2-endo,3-endo-dicarboxylic acid-dimethyl ester (9) with a yield of 82%. The two methyl groups in dimethyl maleic anhydride makes it a weak dienophile which makes Diels-Alder reaction sluggish. The synthetic procedure followed by Kreiser et al. is very tedious involving repeated reactions of the reaction mixture with cyclopentadiene (1). The yields and rate of Diels-Alder reaction are known to show improvement when 5 M lithium perchlorate in diethyl ether (5M LPDE) solution. The reaction of cyclopentadiene and 2,3-dimethyl maleic anhydride (7) was, therefore, performed in 5M LPDE at room temperature followed by subsequent reduction with Pd on carbon gave the norbornane anhydride (8) with a yield of 50%. (Scheme 5.3). The anhydride could not be hydrolyzed by the method of Kreiser et al. Hence it was converted to the ester by refluxing with thionyl chloride in presence of methanol which gave a mixture of anhydride and diester (9). The diester was separated from anhydride by dissolving in hexane. Evaporation of hexane gave a white crystalline solid with a yield of 76%. The separation of the anhydride from the diester was monitored by IR and GC. IR shows carbonyl peak for DMNBDA at 1850, 1830 (doublet) and for ester at 1733 cm⁻¹. GC shows the peak for DMNBDA at 7.68 min and DMNBDE at 6.45 min. The IR spectrum of the ester (DMNBDE) (9) is shown in Figure 5.3. The ¹H and ¹³C NMR of DMNBDE (9) is shown in Figures 5.4 and 5.5.
Scheme 5.3 Synthesis of 2-exo,3-exo-dimethyl bicyclo[2.2.1]heptane-2-endo,3-endo-dicarboxylic acid-dimethyl ester (DMNBDE)

Figure 5.3 IR spectrum of 2-exo,3-exo-dimethyl bicyclo[2.2.1]heptane-2-endo,3-endo-dicarboxylic acid-dimethyl ester (DMNBDE)
5.4.2 Synthesis and structure of polyester and copolyesters containing NBDM

5.4.2.1 Synthesis of poly (2,3-norbornane dimethylene terephthalate) (PNBDT) and copolyesters from 2-endo,3-endo--NBDM

2-endo,3-endo--NBDM (6) did not undergo melt polymerization with DMT. High temperature solution polymerization (Scheme 5.4) of NBDM with terephthaloyl chloride
in NMP at 200°C gave a semicrystalline polymer with an inherent viscosity of 0.2 dL/g. There was no improvement in molecular weight after solid state polymerization.

Scheme 5.4 Synthesis of poly (2,3-norbornane dimethylene terephthalate) (PNBDT) from 2-endo,3-endo-NBDM by solution polymerization

Melt copolymerization of DMT, BD and 2-endo,3-endo-NBDM gave polymer with inherent viscosity of 0.16 dL/g and there was no further increase in molecular weight. Melt condensation of the oligomer (obtained by solution polymerization) with BD and DMT gave the homopolymer, PBT.

5.4.2.2 Synthesis and structure of poly (2, 3-norbornane dimethylene terephthalate) (PNBDT) from 2-exo, 3-endo-NBDM

PNBDT (11) was synthesized from 2-exo, 3-endo bis(hydroxymethyl) bicyclo[2.2.1]heptane (4) and DMT by melt condensation using titanium isopropoxide catalyst and the synthesis is illustrated in Scheme 5.5. The polyester was found to be soluble in chloroform. The inherent viscosity of the polyester was found to be 0.33 dL/g and the number average and weight average molecular weights were found to be 18,300 and 32,700 respectively. There was no improvement in molecular weight by melt and solid state polymerization.

The structure of the polyester was confirmed by \(^1\)H and \(^{13}\)C NMR spectroscopy. Figure 5.6 shows the \(^1\)H NMR of PNBDT (11) along with the assignments for the peaks. The peak at 8.1 is assigned to the terephthalate protons, H_6, and the OCH_2 protons, H_c, appears at 4.2-4.4 ppm.
Scheme 5.5 Synthesis of poly (2,3-norbornane dimethylene terephthalate) (PNBDT)

Figure 5.6 $^1$H NMR spectrum of poly (butylene 2,3-norbornane dimethylene terephthalate) (PNBDT)
Figure 5.7 $^{13}$C NMR spectrum of poly (butylene 2,3-norbornane dimethylene terephthalate) (PNBDT)

The $^{13}$C NMR spectrum of PNBDT (11) and the peak assignments is shown in Figure 5.7. The carbonyl carbon, $C_h$, appears at 166.71 and 166.74 ppm; the $C_e$ carbons at 68.5 and 66.9 ppm.

5.4.2.3 Synthesis and structure of poly (butylene terephthalate-co-norbornane dimethylene terephthalate) copolyesters (P(BT-co-NBDT))

Copolyesters of dimethyl terephthalate and 1,4-butanediol containing 2-exo,3-endo-NBDM (4) were synthesized by melt condensation (Scheme 5.6). A series of copolyesters were synthesized by changing the molar ratio of BD/NBDM (90/10, 80/20 and 50/50). The transesterification reactions were carried out at 180-230°C for 6-8 h followed by polycondensation at 230-260°C for 8-11 h. The viscosities of the polyesters were in the range of 0.3-0.4 dL/g.

The structure of the copolyester was confirmed by $^1$H and $^{13}$C NMR spectroscopy. The $^1$H NMR spectrum of PBT$_{55}$NBDM$_{45}$ copolymer with assignments for each peak is shown in Figure 5.8. Table 5.1 gives the peak positions of PBT, PNBDT and PBT$_{55}$BCP$_{45}$ copolyester. In the $^1$H NMR spectrum of the P(BT-co-NBDT) (12) copolyester, the OCH$_2$ protons ($H_d$) is splits into four peaks. The copolyester compositions were calculated from the $^1$H MNR spectra and are given in Table 5.2.
Scheme 5.6 Synthesis of poly (butylene terephthalate-co-norbomane dimethylene terephthalate) (P(BT-co-NBDT))

Table 5.1 $^1$H and $^{13}$C NMR chemical shifts (δ in ppm) of PBT, PBNB and poly(BT-co-NBDT) copolyesters

<table>
<thead>
<tr>
<th>$^1$H Chemical shifts</th>
<th>$^1$H Chemical shifts</th>
</tr>
</thead>
<tbody>
<tr>
<td>B H₉</td>
<td>B Hₐ</td>
</tr>
<tr>
<td>PBT</td>
<td>2.02</td>
</tr>
<tr>
<td>PtNBDT</td>
<td>1.1-1.8</td>
</tr>
<tr>
<td>PBT₃₃NBDT₄₅</td>
<td>1.97</td>
</tr>
</tbody>
</table>

$^{13}$C Chemical Shifts

<table>
<thead>
<tr>
<th>$^{13}$C Chemical Shifts</th>
<th>$^{13}$C Chemical Shifts</th>
</tr>
</thead>
<tbody>
<tr>
<td>C C</td>
<td>C C</td>
</tr>
<tr>
<td>PBT</td>
<td>65.9</td>
</tr>
<tr>
<td>PBT₃₃NBDT₄₅</td>
<td>45.44, 67.9,</td>
</tr>
<tr>
<td>PNBBDT</td>
<td>43.43,</td>
</tr>
</tbody>
</table>

An expanded $^1$H NMR spectrum in the range of 4-5 ppm is shown in Figure 5.9, where the four peaks are assigned to BB (4.43 ppm), BNB (4.41 ppm), NBB (4.32 ppm) and NBNB (4.22 ppm) diads. The peaks arising due to the BB and BNB diads could not be
separated. Hence, the copolyester sequence length and randomness could not be calculated.

Table 5.2 Composition of poly(BT-co-NBDT) copolymers determined by $^1$H NMR

<table>
<thead>
<tr>
<th>Copolyester</th>
<th>Feed composition (mol %)</th>
<th>Copolymer composition$^a$ (mol %)</th>
<th>$\eta_{inh}^b$ dL/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBT</td>
<td>100 0</td>
<td>100 0</td>
<td>0.9</td>
</tr>
<tr>
<td>PBT$<em>{91}$NBDT$</em>{9}$</td>
<td>90 10</td>
<td>91 09</td>
<td>0.30</td>
</tr>
<tr>
<td>PBT$<em>{83}$NBDT$</em>{17}$</td>
<td>80 20</td>
<td>83 17</td>
<td>0.25</td>
</tr>
<tr>
<td>PBT$<em>{52}$NBDT$</em>{48}$</td>
<td>50 50</td>
<td>52 48</td>
<td>0.27</td>
</tr>
<tr>
<td>PNBBDT</td>
<td>0 100</td>
<td>0 100</td>
<td>0.33</td>
</tr>
</tbody>
</table>

$^a$Calculated from $^1$H NMR; $^b$Measured in 60/40 phenol/TCE (w/w) at 30°C.

Figure 5.8 $^1$H NMR spectrum of PBT$_{52}$NBDT$_{48}$ and its peak assignment
Figure 5.9 $^1$H NMR spectra in the range of 4.0-5.0 ppm of (a) PBT, (b) PBT$_9$NBDT$_9$ (c) PBT$_{11}$NBDT$_{17}$ (d) PBT$_{12}$NBDT$_{48}$ (e) PNBDT

The $^{13}$C NMR spectrum of PBT$_{12}$NBDT$_{48}$ is shown in Figure 5.10. The quaternary carbon of the terephthalate, C$_9$, appears as a singlet at 133.90 ppm. In the case of the
poly(BT-co-NBDT) (12) copolyesters the quaternary carbon does not split into four signals as in the case of poly(BT-co-CT) and poly(BT-co-CPDT) copolyesters.

5.4.2.4 Crystallization and melting behavior

PNBDT (10) synthesized by solution polymerization exhibits melting endotherm at 214°C on heating in DSC. However it does not crystallize on subsequent cooling or on heating. It appears that the PNBDT underwent solvent induced crystallization during the course of precipitation. The sample shows a T_g of 123°C. On the other hand the polyester synthesized from 2-exo,3-endo-NBDM, namely, PNBDT (11) has a T_g of 113°C and is found to be amorphous. The copolyesters were synthesized from 2-exo,3-endo-NBDM. Copolyesters rich in PBT show distinct melting endotherm indicating their ability to crystallize. When the PNBDT composition increases above 20% the copolyesters lose their ability to crystallize. Figure 5.11 shows the thermograms of the crystallizable samples during heating and subsequent cooling. The melting temperature, heat of fusion, crystallization temperature and the heat of crystallization for the copolyesters are given in Table 5.3. The rapid decrease in T_m and T_c is indicative of eutectic crystallization behavior but only a small portion of the range is realized. The T_g on the other hand exhibits a linear change from 40 to 113°C with increase in PNBDT composition.

Table 5.3 Thermal properties of poly(butylene-co-norbormane dimethylene terephthalate) (poly(BT-co-NBDT)) copolyesters

<table>
<thead>
<tr>
<th>Polyester sample</th>
<th>( \eta_{inh} ) (dL/g)</th>
<th>T_g (°C)</th>
<th>T_m (°C)</th>
<th>( \Delta H_m ) (J/g)</th>
<th>T_mc (°C)</th>
<th>( \Delta H_c ) (J/g)</th>
<th>IDT (^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBT</td>
<td>0.60</td>
<td>40</td>
<td>226</td>
<td>41</td>
<td>193</td>
<td>49</td>
<td>374</td>
</tr>
<tr>
<td>PBT_{90}NBDT_{9}</td>
<td>0.30</td>
<td>47</td>
<td>211</td>
<td>36</td>
<td>175</td>
<td>43</td>
<td>385</td>
</tr>
<tr>
<td>PBT_{85}NBDT_{17}</td>
<td>0.25</td>
<td>58</td>
<td>190</td>
<td>28</td>
<td>143</td>
<td>40</td>
<td>380</td>
</tr>
<tr>
<td>PBT_{12}NBDT_{48}</td>
<td>0.27</td>
<td>75</td>
<td>Amorphous</td>
<td>380</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PNBDT</td>
<td>0.33</td>
<td>113</td>
<td>Amorphous</td>
<td>395</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Measured in 60/40 phenol/TCE (w/w) at 30°C; \(^b\) Measured by TGA
The WAXD patterns (Figure 5.12) shows that the copolyesters with PNBDT compositions higher than 20% are amorphous. The copolyesters that crystallize clearly display diffraction pattern similar to that of PBT. The d-spacings of the reflections plotted in Figure 5.13 show little variation indicating that the copolyesters crystallized in the PBT lattice. Detailed sequence analysis could not be performed on these copolyesters, but based on the results obtained on other copolyesters studied in the chapters 3 and 4, it is assumed that these copolyesters are also random in nature and have similar sequence length. The length of NBDT units were calculated using conjugate gradient and Newton-
Raphson method using Cerius 2 software was 1.22 nm which was 0.034 nm shorter than the BT unit. The compositions crystallized are rich in PBT and have PBT sequence length.

Figure 5.12 WAXD patterns of poly(BT-co-NBDT) copolyesters

Figure 5.13 Changes of d-spacings for poly(BT-co-NBDT) copolymers as a function of copolymer composition (a) 001(along chain direction), (b) 011, (c) 010, (d) 111 (e) 100 and (f) 111 reflections (based on PBT structure)
greater than 3 (Chapter 3 Table 3.3, Table 3.6). Hence, PBT sequence can crystallize with the rejection of PNBGT to the amorphous phase. The compositions in which NBDT composition was more than 25 %, the sequence length was less than 3 and could not crystallize.

5.4.3 Synthesis and characterization of polyester and copolyesters containing NBDE

5.4.3.1 Synthesis and structure of poly (butylene-2,3-norbonane dicarboxylate) (PBNB)

Poly (butylene-2,3-norbornane dicarboxylate) (PBNB) (13) was synthesized from dimethyl bicyclo[2.2.1]heptane 2-exo,3-endo dicarboxylate (NBDE) (3) and butanediol by melt condensation. The synthetic scheme is illustrated in Scheme 5.7. The transesterification reaction was carried out at 160-180°C for 3 h and polycondensation at 210-260°C for 5 h. The polyester was found to be rubbery. The inherent viscosity was found to be 0.6 dL/g and the number average and weight average molecular weights were found to be 37,000 and 98,800 respectively, with polydispersity 2.65.

![Scheme 5.7 Synthesis of poly (butylene-2,3-norbornane dicarboxylate) (PBNB)](image)

The structure of the polyester was confirmed by $^1$H and $^{13}$C NMR spectra.
Figure 5.14 $^1$H NMR spectrum with peak assignments of poly (butylene norborne dicarboxylate) (PBNB)

Figure 5.15 $^{13}$C NMR spectrum of poly(butylene norborne dicarboxylate) (PBNB)
The $^1$H NMR spectrum of PBNB (13) and the repeat units along with the assignments is shown Figure 5.14. The peak at 4.11, $H_e$, is assigned to the OCH$_2$ protons. The peaks at 3.22 and 2.82, $H_d$, to the CH protons attached to the carbonyl group. The bridgehead protons, $H_c$, are non-equivalent and appear at 2.64 and 2.56 ppm. The chemical shifts are given in Table 5.4. In the $^{13}$C NMR spectrum of PBNB (Figure 5.15), the carbonyl carbon, $C_g$, appears at 173.2 and 174.39 (trans carbonyl). The carbon attached to oxygen, $C_d$, appears at 63.88 and 64.0 ppm.

### 5.4.3.2 Synthesis and structure of poly (butylene terephthalate-co-2,3-norbornane dicarboxylate) (Poly(BT-co-BNB)) copolyesters

Copolymers of dimethyl terephthalate and 1,4-butanediol containing NBDE were synthesized by melt condensation (Scheme 5.8). A series of copolyesters were synthesized by changing the molar ratio of DMT/NBDE (90/10, 80/20, 70/30 and 50/50). The copolyesters containing up to 30% PBNB were found to be insoluble in chloroform, whereas the copolyester containing 50% PBNB was found to be soluble. The inherent viscosities were in the range of 0.8 - 1.4 dL/g. The $M_n$ and $M_w$ of PBT$_{30}$NB$_{50}$ were found to be 51,700 and 88,900 with a dispersity of 1.7.

![Scheme 5.8 Synthesis of poly (butylene terephthalate-co-butylene-2,3-norbornane dicarboxylate) (P(BT-co-BNB))](image)

The structure and the composition of the copolyesters were confirmed by $^1$H and $^{13}$C NMR spectra. Figure 5.16 shows the chemical structure of the copolyester along with
the notations used for assigning the NMR chemical shifts. Table 5.4 summarizes the $^1$H and $^{13}$C NMR chemical shift values of PBT, PBNB and poly(BT-co-BNB) copolyesters. The $^1$H NMR spectra of PBT, PBNB and PBT$_{50}$NB$_{50}$ are shown in Figure 5.17. The OCH$_2$ protons, H$_e$, for PBT appears at 4.5 ppm and for PBNB appears at 4.11 ppm. In the case of the copolyesters the OCH$_2$ protons are split into four corresponding to the different diads possible: TT, TNB, NBT and NBNB, where T is the terephthalate moiety and NB is the norbornane dicarboxylate moiety.

![Chemical structure of poly(BT-co-BNB) copolyester with notations used for NMR assignments](image)

**Figure 5.16** Chemical structure of poly(BT-co-BNB) copolyester with notations used for NMR assignments

Table 5.4 $^1$H and $^{13}$C NMR Chemical Shifts (δ in ppm) of PBT, PBNB and poly(BT-co-BNB) copolyesters

<table>
<thead>
<tr>
<th></th>
<th>$^1$H Chemical shifts</th>
<th></th>
<th>$^{13}$C Chemical Shifts</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$^1$H$_a$</td>
<td>$^1$H$_d$</td>
<td>$^1$H$_g$</td>
</tr>
<tr>
<td>PBT</td>
<td>2.02</td>
<td>4.5</td>
<td>8.12</td>
</tr>
<tr>
<td>PBNB</td>
<td>4.41, 4.47</td>
<td>1.7</td>
<td>1.2-1.9</td>
</tr>
<tr>
<td>PBT$<em>{50}$NB$</em>{50}$</td>
<td>2.0</td>
<td>8.11</td>
<td>1.2-1.7</td>
</tr>
</tbody>
</table>

In the $^1$H NMR spectrum, the peak for TT, ie the repeat unit in which both OCH$_2$ are attached to terephthalate appears at 4.47. The TNB peak appears at 4.41. As the peaks
for NBT and NBNB appear as a broad multiplet from 4.1-4.26 ppm, they could not be resolved. Hence the diad distributions for the copolyesters could not be calculated.

Table 5.5 Composition of poly(BT-co-BNB) copolymers determined by \(^1\)H NMR

<table>
<thead>
<tr>
<th>Copolyester(^a)</th>
<th>Feed composition (mol %)</th>
<th>Copolymer composition(^b) (mol %)</th>
<th>(\eta_{inh})^(b) (dL/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBT</td>
<td>100 0</td>
<td>100 0</td>
<td>0.90</td>
</tr>
<tr>
<td>PBT(<em>{90})NB(</em>{10})</td>
<td>90 10</td>
<td>90 10</td>
<td>0.82</td>
</tr>
<tr>
<td>PBT(<em>{78})NB(</em>{22})</td>
<td>76 24</td>
<td>78 22</td>
<td>0.96</td>
</tr>
<tr>
<td>PBT(<em>{71})NB(</em>{29})</td>
<td>71 29</td>
<td>71 29</td>
<td>1.42</td>
</tr>
<tr>
<td>PBT(<em>{50})NB(</em>{50})</td>
<td>50 50</td>
<td>50 50</td>
<td>0.80</td>
</tr>
<tr>
<td>PBNB</td>
<td>0 100</td>
<td>0 100</td>
<td>0.66(^c)</td>
</tr>
</tbody>
</table>

\(^a\)calculated from \(^1\)H NMR. \(^b\)Measured in 60/40 phenol/TCE (v/v) at 30°C; \(^c\) measured in chloroform

Figure 5.17 \(^1\)H NMR spectra of (A) PBT, (B) PBT\(_{50}\)NB\(_{50}\), (C) PBNB
The $^{13}$C NMR spectrum of PBT$_{50}$NB$_{50}$ is shown in Figure 5.18. The peak for carbonyl carbon of the norbornane dicarboxylate, C_g, appears at 174.29 and 174.48 ppm and that for terephthalate appears at 165.57 ppm. The peak for OCH$_2$ carbon, C_e, attached to terephthalate appears at 64.74 and that attached to norbornane dicarboxylate appears at 63.92 and 64.04 ppm.

5.4.3.3 Thermal properties

Poly (butylene norbornane dicarboxylate) (PBNB) (13) is an amorphous polyester with a $T_g$ of 15°C. Among the copolymers only the PBT rich compositions crystallize and the thermograms during heating and cooling are shown in Figure 5.19. The parameters extracted from the thermograms are given in Table 5.6. The $T_m$, $T_c$ and $T_g$ are plotted in Figure 5.20 and all exhibit a linear change with composition. The heat of fusion and crystallization also decrease indicating the difficulty in crystallizing with increase in PBNB content.
Table 5.6 Thermal properties of poly(BT-co-BNB) copolyesters.

<table>
<thead>
<tr>
<th>Polyester</th>
<th>$\eta_{inh}^a$</th>
<th>$T_g$</th>
<th>$T_m$</th>
<th>$\Delta H_m$</th>
<th>$T_c$</th>
<th>$\Delta H_c$</th>
<th>IDT$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$(^\circ C)$</td>
<td>$(^\circ C)$</td>
<td>$(J/g)$</td>
<td>$(^\circ C)$</td>
<td>$(J/g)$</td>
<td></td>
</tr>
<tr>
<td>PBT</td>
<td>0.90</td>
<td>40</td>
<td>226</td>
<td>41</td>
<td>193</td>
<td>49</td>
<td>374</td>
</tr>
<tr>
<td>PBT$<em>{90}$NB$</em>{10}$</td>
<td>0.82</td>
<td>38</td>
<td>205</td>
<td>23</td>
<td>157</td>
<td>29</td>
<td>384</td>
</tr>
<tr>
<td>PBT$<em>{78}$NB$</em>{22}$</td>
<td>0.96</td>
<td>34</td>
<td>175</td>
<td>13</td>
<td>113</td>
<td>25</td>
<td>384</td>
</tr>
<tr>
<td>PBT$<em>{72}$NB$</em>{28}$</td>
<td>1.42</td>
<td>28</td>
<td>162</td>
<td>29</td>
<td>93</td>
<td>24</td>
<td>386</td>
</tr>
<tr>
<td>PBT$<em>{50}$NB$</em>{50}$</td>
<td>0.80</td>
<td>22</td>
<td>120</td>
<td>10</td>
<td>does not crystallize</td>
<td></td>
<td>375</td>
</tr>
<tr>
<td>PBNB</td>
<td>0.66</td>
<td>15</td>
<td>Amorphous</td>
<td></td>
<td></td>
<td>389</td>
<td></td>
</tr>
</tbody>
</table>

*Measured in 60/40 phenol/TCE (w/w) at 30°C; $^b$ Measured by TGA

Figure 5.19 DSC heating (A) and cooling (B) thermograms of (a) PBT, (b) PBT$_{90}$NB$_{10}$, (c) PBT$_{78}$NB$_{22}$, (d) PBT$_{72}$NB$_{28}$, (e) PBT$_{50}$BCD$_{50}$
S.4.3.4 X-ray diffraction studies

The WAXS patterns of the copolyesters are shown in Figure 5.21. PBNB (13) is amorphous polyester and is indicated by the broad amorphous pattern (not shown in the Figure). All the compositions with PBT 50% or more show well defined peaks due to crystalline fraction. The composition PBT$_{50}$NB$_{50}$ shows weak diffraction pattern only after annealing at 100°C for about 2 hours. The weak diffraction pattern displayed by PBT$_{50}$NB$_{50}$ composition is indicative of cocrystallization, as the sequence length of PBT is less than 3 it cannot crystallize on its own. The PBNB segment cocrystallizes with PBT in the PBT lattice. The incorporation of BNB unit in the PBT lattice was apparent from the 001 spacing. The 001 d-spacing, which was less susceptible to variation to structure and morphology, showed marginal decrease with increase in BNB content and was in agreement with the BNB unit’s length 1.02 nm (calculated using conjugate gradient and Newton-Raphson method using Cerius 2 software), which was lower than the length of BT unit (1.234 nm). The definite but small change in the d-spacing of the reflections (Figure 5.22) also points to the cocrystallization behavior. The experimental data is a little limiting to conclude the nature of the cocrystallization behavior. Nevertheless, based on the behavior of d-spacing and results obtained in the Chapter 3 and 4, it may be concluded that the crystallization is isomorphic in nature.
Figure 5.21 WAXD patterns of poly(BT-co-BNB) copolyesters

Figure 5.22 Changes of d-spacings for poly(BT-co-BNB) copolymers as a function of copolymer composition (a) 001 (along chain direction), (b) 011, (c) 010, (d) 111 and (e) 100 (f) 111 reflections (based on PBT structure)
5.5 Conclusions

A series of poly(butylene terephthalate-co-2,3-norbomane dimethylene terephthalate) (poly(BT-co-NBDT)) (12) and poly (butylene terephthalate-co-2,3-norbomane dicarboxylate) (poly(BT-co-BNB)) (14) copolymers with various NBT and BNB contents were synthesized by melt condensation. The NMR spectroscopic analysis indicates that the copolymers are random. The thermal analysis and XRD studies shows that the PNBDT (11) is an amorphous polyester with a $T_g$ of 113°C. The Poly(BT-co-NBDT) copolyesters could crystallize in compositions upto 20 % NBDT content, while the composition having 50 % NBDT is amorphous. On the other hand, PBNB (13) was found to be an amorphous polyester with a $T_g$ of 15°C. The poly(BT-co-BNB) copolyesters showed isomorphic crystallization and did not show eutectic behaviour in melting and crystallization. The glass transition temperature showed linear dependency on composition in these copolymers.

The copolyesters of dimethyl terephthalate and 1,4-butanediol exhibit a wide range of melting temperature and glass transition temperature. Incorporation of NBDM as a comonomer, which has a rigid norborne ring increases the $T_g$ of PBT. While incorporation of 2,3-norbomane dicarboxylate comonomer, which is the ester component, results in copolyesters, which have $T_g$, lower than PBT and the $T_m$ does not show eutectic behavior.

II. Synthesis and characterization of copolyesters containing 2,2,4,4-tetramethyl-1,3-cyclobutane diol

5.6 Introduction

Polyesters of 2,2,4,4-tetramethyl-1,3-cyclobutane diol (TMCBD) reported\[7,8,9] are primarily high melting, semicrystalline materials. Melting points for the polyesters from dimethyl terephthalate and TMCBD, are 316-319°C (38/62 cis/trans), 296-308°C (cis) and >350°C (trans)\[10] and the $T_g$ is 174°C. The synthesis of aliphatic polyester containing TMCBD having superior weathering properties has been described\[10]. Polyesters synthesized from TMCBD 1,4-cyclohexanedicarboxylic acid are reported to possess improved weatherability\[11]. The aliphatic copolyesters synthesized from 1,4-CHDA, CHDM and TMCBD have $T_g$ >100°C and improved UV resistance.
This chapter discusses the synthesis and properties of aliphatic copolyesters of TMCBD with cycloaliphatic diesters and a straight chain diol.

5.7 Experimental

5.7.1 Materials

1,4-Dimethyl terephthalate (DMT), (99+%) 1,4-butanediol (BD), ruthenium on carbon and isobutyryl chloride were obtained from Sigma-Aldrich Inc, USA. Triethyl amine, diethyl ether and toluene, were obtained from s.d. fine- chem Limited, Mumbai.

5.7.2 Reagents and purification

DMT was recrystallized from methanol. BD was distilled and stored over molecular sieves. Triethyl amine was stirred over calcium hydride and distilled and stored on KOH. Diethyl ether was kept overnight over calcium chloride, distilled and was refluxed over sodium.

5.7.3 Synthesis of 2,2,4,4-tetramethyl-1,3-cyclobutane diol (TMCBD)

Triethyl amine (120 mL, 0.8 mol) and 160 mL anhydrous diethyl ether were taken in a 1000 mL round bottom flask and cooled in an ice salt mixture. Isobutyryl chloride (15) (52 mL, 0.5 mol) in 80 mL anhydrous diethyl ether was added slowly over 1 h under vigorous stirring. The reaction mixture was brought to room temperature and allowed to stir for 21 days. The reaction mixture was filtered using a sintered funnel and washed several times with diethyl ether. Evaporation of ether gave yellow colored crude 2,2,4,4-tetramethyl cyclobutane dione (16) which was purified by vacuum sublimation to give 10.37 g (60 %) of white crystalline dione. 2,2,4,4-tetramethyl cyclobutane dione (14.9 g, 0.1 mol), 0.9 g of ruthenium on carbon and 50 mL of methanol were charged into a 300 mL stainless steel Parr reactor. The reactor was purged with hydrogen gas and pressurized to 1000 psi of H₂. The reactor was heated to 125°C when hydrogen absorption started. The reaction was continued till there was no more absorption of H₂. The reaction mixture was cooled to room temperature and filtered off to remove ruthenium. Evaporation of methanol gave 14.5 g of TMCBD (17). TMCBD was recrystallized from hot toluene to yield 12.8 g of white crystalline TMCBD. m. p. 124°C (lit¹ 129-150°C).

Elemental, found (calcd.): C - 66.1(66.66), H -11.58 (11.11)

IR (neat) – 3312 (O-H), 2900, 2860, 1490, 1390, 1041, 960, 850 cm⁻¹.
GC-7.13, 7.31 min, 45:55 cis/trans ratio.

\(^1\)H NMR (chloroform) \(\delta\): 0.9(12H, t, CH\(_3\)), 3.15, 3.25(2H, dd CH), 4.5(2H, t, OH)

\(^{13}\)C NMR (chloroform) \(\delta\): 78.4, 77.03 (CH-OH), 42.12, 40.29 (quartemary C), 29.3, 22.9, and 15.78 (CH\(_3\)).

5.7.4 Synthesis of copolyester containing TMCBD, BD with DMT

A 100 mL two-neck round bottom flask equipped with a magnetic stirring bar, nitrogen inlet, air condenser and spiral trap was charged with DMT (2.5 g 0.013 mol), TMCBD (17) (1.19 g, 0.008 mol) and dibutyl tin dioxide (DBTO) (0.1 wt % w. r. t DMT). The flask was degassed with N\(_2\) and heated in an oil bath at 160-210°C for 7 h under N\(_2\) atmosphere (closed condition to avoid sublimation of DMT and TMCBD) when methanol distilled out. The reaction flask was subsequently cooled to room temperature. BD (0.76 g, 8 mmol) and titanium isopropoxide (0.05 wt % w.r.t. DMT) were added to the reaction flask and degassed again. The reaction mixture was heated at 230-250°C for 12 h under a constant flow of N\(_2\). The pressure was gradually reduced to about 0.02 mbar over 30 min and reaction continued at 250-260°C for 6 h. The flask was cooled under vacuum and polymer was dissolved in methylene chloride and precipitated in methanol. The polymer was filtered, washed with methanol and dried in a vacuum oven. The polymer was found to be fluffy (powder). Yield = 3g (90 %).

\(\eta_{inh}\) (chloroform) - 0.5 dL/g

\(^1\)H NMR (CDCl\(_3\)) \(\delta\): 1.33 (12H, t, CH\(_3\)), 2.00 (4H, s, CH\(_2\)), 4.46 (4H, s, CH\(_2\)O) 4.66, 4.81 (2H, d, CH-O), 8.15 (8H, s, aromatic)

\(^{13}\)C NMR (CDCl\(_3\)) \(\delta\): 16.86, 22.72 (CH\(_3\)), 25.39 (CH\(_2\)), 28.44 (CH\(_3\)), 40.47, 41.79 (quartemary C), 64.77 (OCH\(_2\)), 80.58, 81.54 (O-CH), 129.45, 129.56, 133.71, 133.87, 133.94, 134.08 (aromatic), 165.26, 165.58 (CO).

5.7.5 Synthesis of copolyester containing TMCBD, BD with DMCD

A 100 mL two-neck round bottom flask fitted with a magnetic stirring bar, nitrogen inlet, air condenser and spiral trap was charged with DMCD (5.01 g 0.025 mol), TMCBD (2.24 g, 0.016 mol) and dibutyl tin dioxide (DBTO) (0.1 wt % w. r. t DMCD). The flask was degassed with N\(_2\) and heated in an oil bath at 200-230°C for 11 h under N\(_2\) atmosphere when methanol distilled out. And then the reaction flask was cooled to room temperature. BD (1.42 g, 0.0157 mmol) and titanium isopropoxide (0.05 wt % w.r.t. DMCD) were
added to the reaction flask and degassed again. The reaction mixture was heated at 230-
250°C for 4 h under a constant flow of N₂. The pressure was gradually reduced to about
0.02 mbar over 30 min and reaction continued at 250-260°C for 13 h. The flask was
cooled under vacuum and the polymer recovered. Yield = 6.2 g (98 %).

ηₘₙ (chloroform) = 0.65 dL/g

GPC (CHCl₃) Mn = 42, 200 Mₙ = 80,000 (Mₙ/Mₚ = 1.9)

¹H NMR (CDCl₃) δ: 1.10 (12H, t, CH₃), 1.3-2.6 (26H, m, ring), 4.10, (4H, s, OCH₂),
4.27, 4.41 (2H, s, CH-OH)

¹³C NMR (CDCl₃) δ: 16.65, 16.75, 22.5, 22.6, 25.23, 25.91, 27.91, 28.04, 28.36, 39.82,
40.55, 41.16, 42.57, 63.95, 79.43, 79.56, 80.28, 80.44, 174.54, 174.77, 174.96, 175.24.

5.7.6 Synthesis of copolyester containing TMCBD, BD with CPDE

A 100 mL two-neck round bottom flask fitted with a magnetic stirring bar, nitrogen inlet,
air condenser and spiral trap was charged with CPDE (3.74 g, 0.02 mol), TMCBD (1.87
g, 0.013 mol) and dibutyl tin dioxide (DBTO) (0.1 wt % w.r.t CPDE). The flask was
degassed with N₂ and heated in an oil bath gradually from 100-180°C for 4 h under N₂
atmosphere when methanol distilled out. The reaction mixture was further heated at 180-
200°C for 8 h. The reaction flask was cooled to room temperature, BD (1.29 g, 0.014
mol) and titanium isopropoxide (0.05 wt % w.r.t. CPDE) were added to the reaction flask
and degassed again. The reaction mixture was heated at 230-250°C for 4 h under a
constant flow of N₂. The pressure was gradually reduced to about 0.02 mbar over 30 min
and the reaction was continued at 240-250°C for 8.5 h. The polymer was found to be
rubbery. Yield = 4.4 g (92 %).

ηₘₙ (chloroform) = 1.23 dL/g

¹H NMR (CDCl₃) δ: 1.10 (12H, t, CH₃), 1.71 (4H, s, CH₂), 1.8-2.4 (12H, m, ring ), 2.7-
3.1 (4H, m, ring), 4.11(4H, s, CH-OH), 4.28, 4.43 (2H, d, OCH₂)

¹³C NMR (CDCl₃) δ: 16.45, 22.29 (CH₃), 24.88 (CH₂), 28.14 (CH₃), 29.17, 29.90, 32.62,
33.10, 40.10, 41.42, 43.56, 44.14, 43.99, 65.43 (CH₂-OH), 80.95, 81.85 (CH-OH),
177.73, 178.07, 178.49 (CO).

5.7.7 Synthesis of copolyester containing TMCBD, BD with NBDE

A 100 mL two-neck round bottom flask equipped with a magnetic stirring bar, nitrogen
inlet, air condenser and spiral trap was charged with NBDE (4.19 g, 0.0.02 mol), TMCBD
(2.2 g, 0.015 mol) dibutyl tin dioxide (DBTO) (0.1 wt % w.r.t NBDE). The flask was degassed with N\textsubscript{2} and heated in an oil bath at 120-200°C for 6 h under N\textsubscript{2} atmosphere (closed condition to avoid sublimation of TMCBD) when methanol distilled out. The reaction was further continued at 200-220°C for 12 h. The reaction flask was cooled to room temperature, BD (1.35 g, 0.015 mol) and titanium isopropoxide (0.05 wt % w.r.t. NBDE) were added to the reaction flask and degassed again. The reaction mixture was heated at 230-250°C for 4 h under a constant flow of N\textsubscript{2}. The pressure was gradually reduced to about 0.02 mbar over 30 min and reaction continued at 250-260°C for 11 h. The flask was cooled under vacuum and polymer was recovered. Yield = 4.98 g (96 %).

\[ \eta_{inh} \text{(chloroform)} = 0.6 \text{ dL/g} \]

\[ ^1H \text{ NMR (CDCl}_3\text{)} \delta: 0.8-1.9 (28H, m, CH}_3\text{ and ring protons), 2.46-3.0 (6H, m, bridgehead), 3.21 (2H, m, CH-O), 4.11 (4H, s, OCH}_2\text{), 4.24-4.45 (2H, dd, CH-OH) } \]

5.8 Results and discussion

5.8.1 Monomer synthesis

TMCBD was synthesized\textsuperscript{13} from isobutyryl chloride (10), which dimerizes to form dimethyl ketene in presence of triethyl amine base, which spontaneously dimerizes to cyclic diketone (11), a molecule known since 1906 (Scheme 5.9). Hydrogenation of ketone in presence of ruthenium catalyst gives cis/trans-TMCBD (12).

\[ \text{(CH}_3\text{CH}_2\text{)}_3\text{N-COCI} \rightarrow (10) \]

\[ \rightarrow \text{(11)} \]

\[ \text{H}_2, \text{Ru/C} \rightarrow \text{cis/trans} \]

\[ \text{(12)} \]

Scheme 5.9 Synthesis of 2,2,4,4-tetramethyl-1,3-cyclobutane diol (TMCBD)

5.8.2 Synthesis and structure of TMCBD /BD terephthalate copolyester

The copolymers of dimethyl terephthalate and 1,4-butanediol containing cyclobutane diol were synthesized by melt polymerization in two stages (Scheme 5.10). The first stage involved the transesterification of TMCBD with DMT in presence of dibutyltin oxide catalyst. The initial stages of transesterification was carried out under closed
conditions instead of a constant stream of N₂ gas as both DMT and TMCBD underwent sublimation. It has been reported that the tin compounds are good catalysts for transesterification with TMCBD. Since the TMCBD hydroxyl groups are secondary and sterically hindered by adjacent methyl groups, they require longer reaction times. The methanol byproduct was formed after 4-5 h of reaction time at 160-210°C. During the second trans-esterification stage, BD was added and melt polymerization carried out in the presence of titanium isopropoxide as catalyst. The excess diols were removed by heating at 230-260°C under high vacuum to increase the molecular weight. The polymer was dissolved in methylene chloride, precipitated in methanol and filtered.

Scheme 5.10 Synthesis of TMCBD /BD terephthalate copolyester

The \(^1\)H NMR spectrum is shown in Figure 5.23. The TMCBD /BD molar ratio in the final polymer was calculated from the H\(_b\) (4.44) and H\(_d\) (4.66, 4.81) protons and was found to be the same as the TMCBD /BD ratio in the monomer feed. The NMR of the copolymer also showed the same cis/trans ratio as in the feed. The \(^13\)C NMR spectrum of the copolyester is shown in Figure 5.24. The peak for carbonyl carbon appears at 165.58 and 165.26 for terephthalate attached to BD and TMCBD respectively. The C\(_b\) carbon appears at 64.77 and C\(_d\) carbon appears at 80.58 and 81.54 for the cis and trans isomers. The tetra methyl groups show peaks at 16.86 and 28.44 for the cis isomer and at 22.72 for the trans isomer.
Figure 5.23 $^1$H NMR spectrum of TMCBD/BD terephthalate copolyester

Figure 5.24 $^{13}$C NMR spectrum of TMCBD/BD terephthalate copolyester
5.8.3 Synthesis of TMCBD/BD cyclohexane dicarboxylate copolyester

Aliphatic cyclohexane dicarboxylate copolyester containing TMCBD/BD was synthesized from dimethyl-1,4-cyclohexane dicarboxylate, BD and TMCBD by melt polymerization using dibutyltin oxide and titanium isopropoxide as catalysts in two stages (Scheme 5.11). The amorphous copolyester was transparent and slightly yellow in color when cooled from the melt to room temperature. The inherent viscosity of the copolyester was found to be 0.65 dL/g and the $M_n$ and $M_w$ were found to be 42,200 and 80,000 respectively.

Scheme 5.11 Synthesis of TMCBD/BD cyclohexane dicarboxylate copolyester

The TMCBD/BD ratio in the copolyester was calculated from the h (4.10 ppm) and d (4.27, 4.41 ppm) proton resonance ($^1$H NMR spectra Figure 5.25). The ratio of TMCBD/BD was found to be 50/50 the same as in the feed. The $^{13}$C NMR spectrum along with the assignments is shown in Figure 5.26. The NMR spectrum shows peak for the h carbons at 63.65 and d carbons at 80.28 and 80.44 ppm.
Figure 5.25 $^1$H NMR spectrum of TMCBD/BD cyclohexane dicarboxylate copolyester

Figure 5.26 $^{13}$C NMR spectrum of TMCBD/BD cyclohexane dicarboxylate copolyester
5.8.4 Synthesis and structure of TMCBD/BD cyclopentane dicarboxylate copolyester

TMCBD/BD copolyester of cyclopentane dicarboxylate was synthesized from dimethyl-1,3-cyclopentane dicarboxylate, BD and TMCBD by melt polymerization using a combination of catalysts, DBTO and titanium isoprooxide (Scheme 5.12). The copolyester was found to be brown colored and rubbery. The inherent viscosity of the copolyester was found to be 1.23 dL/g.

Scheme 5.12 Synthesis of TMCBD/BD cyclopentane dicarboxylate copolyester
Figure 5.27 $^1$H NMR spectra of TMCBD/BD cyclopentane dicarboxylate copolyester

The TMCBD/BD ratio in the copolyester was calculated from the h (4.11) and d (4.28, 4.43) proton resonances (Figure 5.27) and was found to be 50/50. $^{13}$C NMR spectrum (Figure 5.28) shows peaks for h carbons at 65.43 and d carbons at 80.05 and 81.85 ppm.
5.8.5 Synthesis and structure of TMCBD/BD norbornane dicarboxylate copolyester

TMCBD/BD copolyester of norbornane dicarboxylate was synthesized from NBDE, BD and TMCBD by melt polymerization using a combination of catalysts, DBTO and titanium isopropoxide (Scheme 5.13). The copolyester was found to be brown colored. The inherent viscosity of the copolyester was found to be 0.6 dL/g.

![Scheme 5.13 Synthesis of TMCBD/BD norbornane dicarboxylate copolyester](image)

Figure 5.29 shows the $^1$H spectrum of the copolyester. The TMCBD/BD molar ratio in the copolyester was calculated from the h and d proton resonances and was found to be 50/50, same as in the feed.
5.8.6 Thermal properties

All the copolyesters were found to be amorphous and had good thermal stability. The TMCBD/BD terephthalate copolyester has a $T_g$ of 86°C. TMCBD/BD terephthalate copolyester has been synthesized by Kelsey et al. The $T_g$ of the copolyesters having 78/22, 72/28 and 64/36 compositions is 145, 129 and 119 respectively. Using Flory Fox equation the $T_g$ for the TMCBD/BD terephthalate (50/50) copolymer would be 92 °C. In the case of the other copolyesters containing cyclopentane, cyclohexane and norbornane dicarboxylates, incorporation of rigid TMCBD group increases the $T_g$ by 46°C. The $T_g$ and the initial decomposition temperature values are given in Table 5.7.
Table 5.7 Thermal properties of TMCBD/BD copolyesters

<table>
<thead>
<tr>
<th>Diester component</th>
<th>TMCBD/BD mole ratio</th>
<th>$T_g$</th>
<th>IDT$^a$</th>
</tr>
</thead>
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<tr>
<td>[Diagram]</td>
<td>50/50</td>
<td>86</td>
<td>394</td>
</tr>
<tr>
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<tr>
<td>[Diagram]</td>
<td>0/100</td>
<td>15</td>
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</tr>
</tbody>
</table>

$^a$Calculated from TGA

5.9 Conclusions

Aliphatic copolyesters based on cyclobutane diol and butane diol containing, dimethyl terephthalate, 1,4-cyclohexane dicarboxylate, 1,3-cyclopentane dicarboxylate and 2,3-norbornane dicarboxylate were synthesized and found to be amorphous. The incorporation of the rigid cyclobutane diol in the copolymer backbone boosts the $T_g$ by about 40°C compared to the corresponding homopolymers.

5.10 References


