SHORT COMMUNICATION

Synthesis and Characterisation of Bis-(chloromethyl) Oxetane, its Homopolymer and Copolymer with Tetrahydrofuran

T.S. Reddy, K.K. Jayakumar, J.K. Nair, R.S. Satpute, and T. Mukundan

High Energy Materials Research Laboratory, Pune– 411 021

ABSTRACT

Bis-(chloromethyl) oxetane (BCMO) was synthesised from pentaerythritol by chlorination, followed by ring closure. It was polymerised using BF_3-etherate and butanediol system, similarly the BCMO–THF (tetrahydrofuran) copolymer was also synthesised. The monomers and the polymers were characterised by IR, ^1H-NMR and molecular weight. Flame retardant properties of the poly-BCMO were also investigated.

Keywords: Poly-BCMO, BCMO–THF copolymer, HTPB, flame retardant, limiting oxygen index, filler, tetrahydrofuran copolymer, energetic binders, propellant binders, energetic polymers, bis-(chloromethyl) oxetane, thermoplastic elastomers

1. INTRODUCTION

Recent advances in the field of energetic binders for propellants, explosives, and pyrotechnics have resulted in the development of energetic polymers[1]. These polymers have high positive heat of formation, controlled molecular weight, low-glass transition temperature, and narrow polydispersity. Moreover, these can also form thermoplastic elastomers[2], which offer high potential recyclable binder systems.

Energetic polymers generally contain azido, nitro, or nitrato groups in their structures. Glycidyl azide polymer (GAP) and polymers of bis-(azido methyl) oxetane (BAMO), nitrato methyl methyloxetane (NIMMO), and glycidyl nitrate (GLYN) are well-known energetic polymers. Azido polymers are generally prepared from halo precursors. BAMO is prepared from the azidation of its halo precursor, bis-(chloromethyl) oxetane[3] (BCMO). Likewise, the homopolymer of BCMO, ie, poly-BCMO can be treated with sodium azide to obtain poly-BAMO. However, being a solid, poly-BAMO cannot be used for thermoset binder applications. The copolymer of BAMO with tetrahydrofuran (THF) is a viscous liquid and is an excellent candidate for binder applications due to its energetic BAMO moiety coupled with THF, which contribute to good mechanical properties. The precursor of the above copolymer is again a halo polymer, ie, the BCMO-THF copolymer.

Further poly-BCMO contains ~ 45 per cent of chlorine, and it is a potential flame-retardant. Hydroxyl-terminated polybutadiene (HTPB)-based compositions are used for applications like the propellant inhibitor. These systems use inorganic flame-retardant fillers like Sb_2O_3. These solid fillers suffer from disadvantages like settling during curing, phase separation in storage, etc. Poly-BCMO being a fluffy solid material does not suffer from such drawbacks.

Also, being a hydroxyl-terminated polymer, poly-BCMO can crosslink along with HTPB. This paper describes the synthesis and characterisation of BCMO, its homopolymer and copolymer with THF, and studies on poly-BCMO as a flame retardant in HTPB-based systems.

2. EXPERIMENTAL PROCEDURE

2.1 Materials

Pentaerythritol (98 %), tetrahydrofuran (99 %), sodium chloride, ammonium hydroxide, and sodium hydroxide were of qualigens make, while N, N-dimethyl formamide, dichloromethane, and sodium sulphate anhydrous were of S.D. Fine-chem Ltd. Also, thionyl chloride (98 %, Thomas Baker), boron trifluoride-etherate (48 %), and 1,4-butanediol (98 %) were of Fluka make; 1, 1, 1-tris hydroxymethyl propane (TMP) (TCI, Japan) and HTPB (Anabond) having molecular weight of 2800 were used as received.

2.2 Methods of Synthesis

#### 2.2.1 Synthesis of 3,3-bis-(chloromethyl) Oxetane

BCMO was prepared as per the method reported by Stockel[4]. N, N-dimethyl formamide (DMF) was treated with thionyl chloride to produce the Vilsmeier reagent, which selectively yields monochlorohydrin of pentaerythritol. Further, chlorination with thionyl chloride gave pentaerythritol trichlorohydrin which underwent cyclisation to yield BCMO.

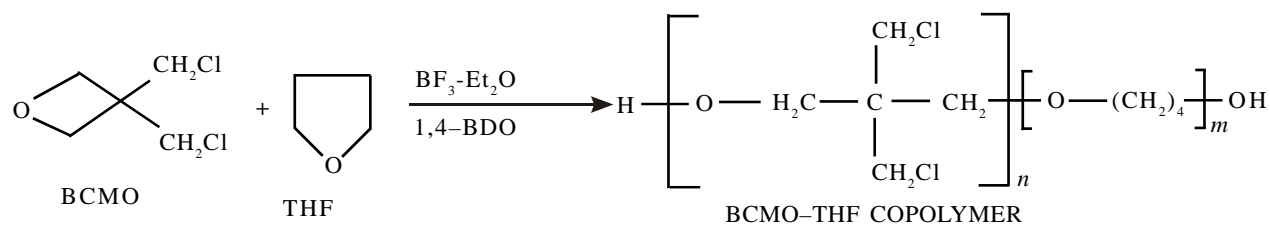#### 2.2.2 Synthesis of Poly-3,3-bis-(chloromethyl) Oxetane

Poly-BCMO was prepared[5] by cationic polymerisation using BF_3-etherate as catalyst and water as co-catalyst. In this method, methylene chloride was used as solvent and 1,1,1-tris hydroxymethyl propane (TMP) as the hydroxyl-terminating agent.
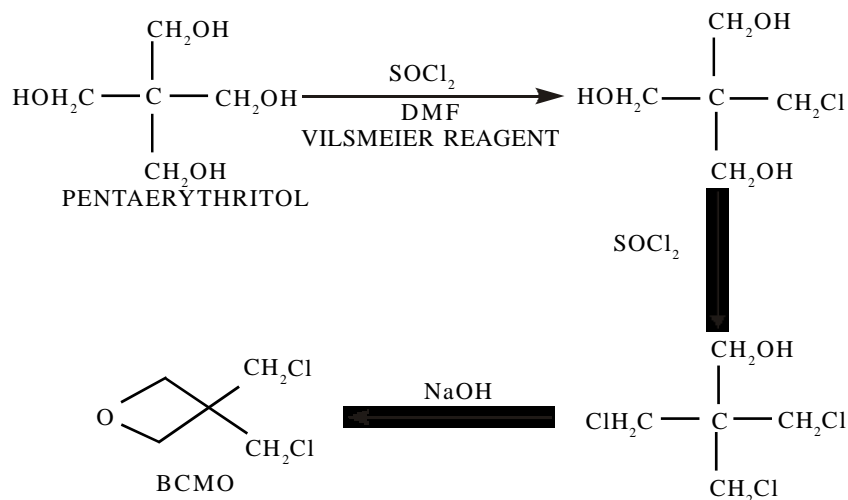
Scheme 1. Synthesis of BCMO
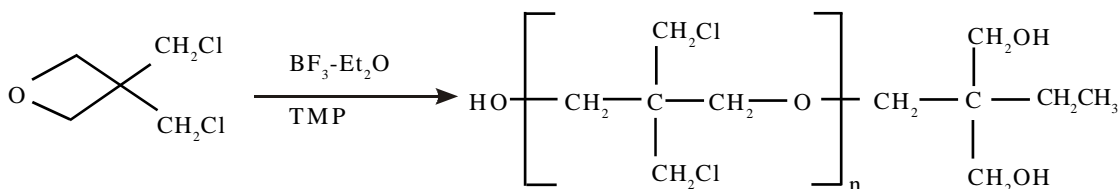
Scheme 2. Synthesis of poly-BCMO

Scheme 3. Synthesis of BCMO–THF copolymer

For the preparation of poly-BCMO, boron trifluoride etherate [5.62 g (0.04 mole)], water [0.036 g (0.002 mole)] and TMP [1.74 g (0.013 mole)] were added to the dry methylene chloride and the suspension was stirred for 15 min. BCMO [31 g (0.20 mole)] was then added in one portion and the mixture was stirred for 18 h at 25 °C. Reaction was terminated using concentrated ammonium hydroxide. Methylene chloride was then removed under vacuum and residual white polymer was washed in succession with methanol. The polymer was dried under vacuum. The yield of poly-BCMO was 71 per cent (22 g).

2.2.3 *Synthesis of 3,3-bis-(chloromethyl) Oxetane-tetrahydrofuran Copolymer*

BCMO-THF copolymer was prepared[6,7] by cationic polymerisation using BF_3-etherate as catalyst. In this method, methylene chloride was used as the solvent and 1,4-butanediol as the initiator.

For the synthesis of BCMO-THF copolymer, BF_3-etherate [5.62 g (0.04 mole)] and BDO [1.62 g (0.018 mole)] were added to dry methylene chloride (15 ml) and the suspension was stirred

for 15 min. Then, THF [7.2 g (0.1 mole)] was added slowly and the temperature was reduced to -10 °C and BCMO [15.5 g (0.1mole)] was added and stirring was continued for 24 h at room temperature. The polymerisation was quenched with saturated sodium chloride solution and washed with water, followed by sodium bicarbonate. The methylene chloride was removed under vacuum and the polymer was precipitated using methanol. The overall yield of the polymer was ~60 per cent.

3. FLAME RETARDANCY

Flame retardancy was determined by limiting oxygen index (LOI) method. Compositions of the flame-retardant formulations are given in Table 1. The HTPB was used as a base and the various percentages of the fillers used were 5 per cent, 10 per cent, and 15 per cent. Each formulation was stirred and kept in vacuum for removing volatiles. The formulations were cured at 60 °C for 8 days and the mechanical properties were determined.

4. CHARACTERISATION

The IR spectra of monomer and copolymer prepared were recorded by smear method using a Perkin-Elmer FTIR spectrophotometer, model: 1605. The IR spectrum of poly-BCMO was recorded in KBr matrix.

^1H-NMR spectra were recorded on a 300 MHz Bruker spectrometer. Tetramethyl silane (TMS) was used as an internal standard and chloroform *d* ($CDCl_3$) as the solvent.

Differential scanning calorimetery (DSC) experiments were carried out on a Perkin-Elmer, Delta para series DSC-7 at 10 °C/min under nitrogen atmosphere. Typical sample mass used was 2 mg.

Table 1. Composition of the flame retardant containing formulations

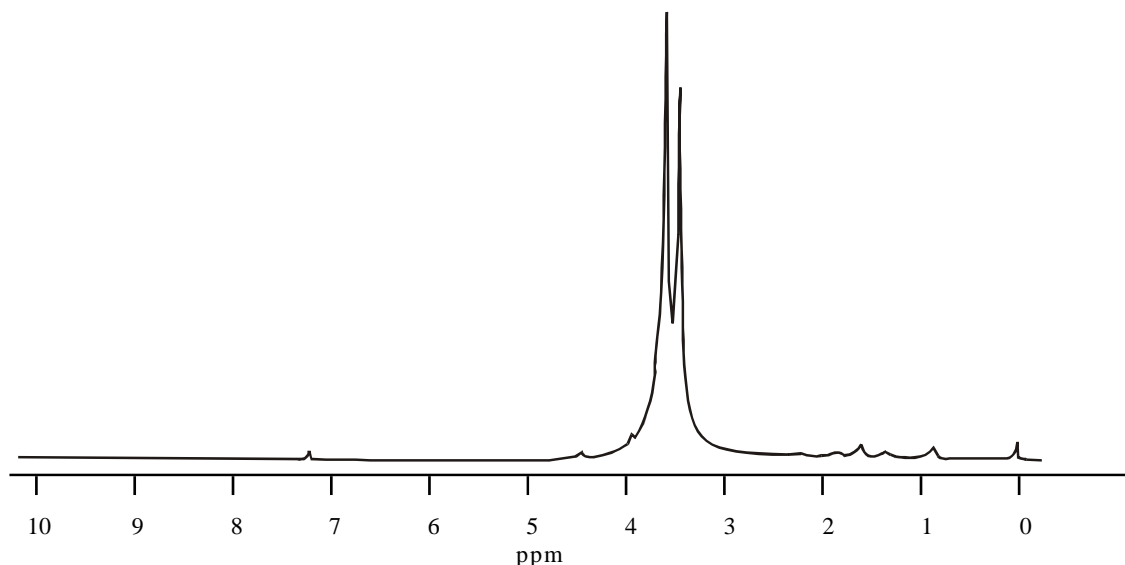| Sample No.	HTPB (g)	Sb_2O_3 (g)	Poly-BCMO (g)	Chlorine content (%)	TDI (g)
1	50.0	-	-		3.1
2	47.5	2.5 (5 %)	-		3.1
3	45.0	5.0 (10 %)	-		3.1
4	42.5	7.5 (15 %)	-		3.1
5	47.5	-	2.5 (5 %)	2.3	3.1
6	45.0	-	5.0 (10 %)	4.6	3.1
7	42.5	-	7.5 (15 %)	6.9	3.1

Figure 1. ^1H-NMR of poly-BCMO

TGA was recorded on a Mettler Toledo STAR instrument in nitrogen atmosphere with a sample mass of 10 mg and at 10 ºC/min. Mechanical properties were tested according to the standard ASTM D-638 using Instron, 1185 universal testing machine with a strain rate of 300 mm/min.

Number average molecular weight was determined on KANUER vapour pressure osmometer.

5. RESULTS & DISCUSSION

BCMO was synthesised by a tedious process in about 60 per cent yield. Subsequently, poly-BCMO and BCMO-THF copolymer were also synthesised in good yield. The monomer, polymer, and the copolymer were characterised by IR, NMR, DSC, and molecular weight.

5.1 Spectral Analysis

*Poly-*3,3-*bis-(chloromethyl) oxetane*

The IR spectrum of poly-BCMO shows absorption peaks[8] due to *C-H* of (-*OCH$_2$*), *C-O, C-C, C-Cl,* and *C-H* (-*CH$_2$Cl*) stretching at 2880 cm^{-1}, 1050 cm^{-1}, 1118 cm^{-1}, 746 cm^{-1}, and 2968 cm^{-1}, respectively. A band at 3428 cm^{-1} appears due *to O-H* stretching of TMP. The *^1H*-NMR spectrum of poly-BCMO is

shown in Fig. 1. The values are reported in δ ppm. It shows a triplet at δ 0.85 (*CH$_3$* of TMP), a multiplet at δ 1.59 (*CH$_2$* of TMP), a multiplet at δ 3.45 (*CH$_2$Cl*), and another multiplet at δ 3.58 (*OCH$_2$*).

BCMO-THF Copolymer

The IR spectrum of BCMO-THF copolymer shows the absorption peaks due to *C-H* of (-*OCH$_2$*), *C-O, C-C, C-Cl,* and *C-H* (-*CH$_2$Cl*) stretching at 2876 cm^{-1}, 1048 cm^{-1}, 1112 cm^{-1}, 732 cm^{-1} and 2956 cm^{-1}, respectively. A band at 3460 cm^{-1} appears due to *O-H* stretching. The ^1H-NMR spectrum of the BCMO-THF copolymer is shown in Fig. 2. It shows a singlet at δ 1.61 (*CH$_2$* of THF) and broad peaks at δ 3.94 and δ 3.66 corresponding to *OCH$_2$* (of BCMO, of THF, and BDO) and *CH$_2$Cl,* respectively. The number average molecular weight of the copolymer was found to be 1342 by vapour-pressure osmometer.

5.2 Mechanical Properties of HTPB Formulations

The mechanical properties of HTPB formulations containing poly-BCMO and *Sb$_2$O$_3$* as filler, are presented in Table 2. The cured samples of poly-BCMO-filled HTPB had better mechanical properties than *Sb$_2$O$_3$*-filled HTPB. Poly-BCMO is a hydroxyl-terminated polymer. Hence, it appeared that it
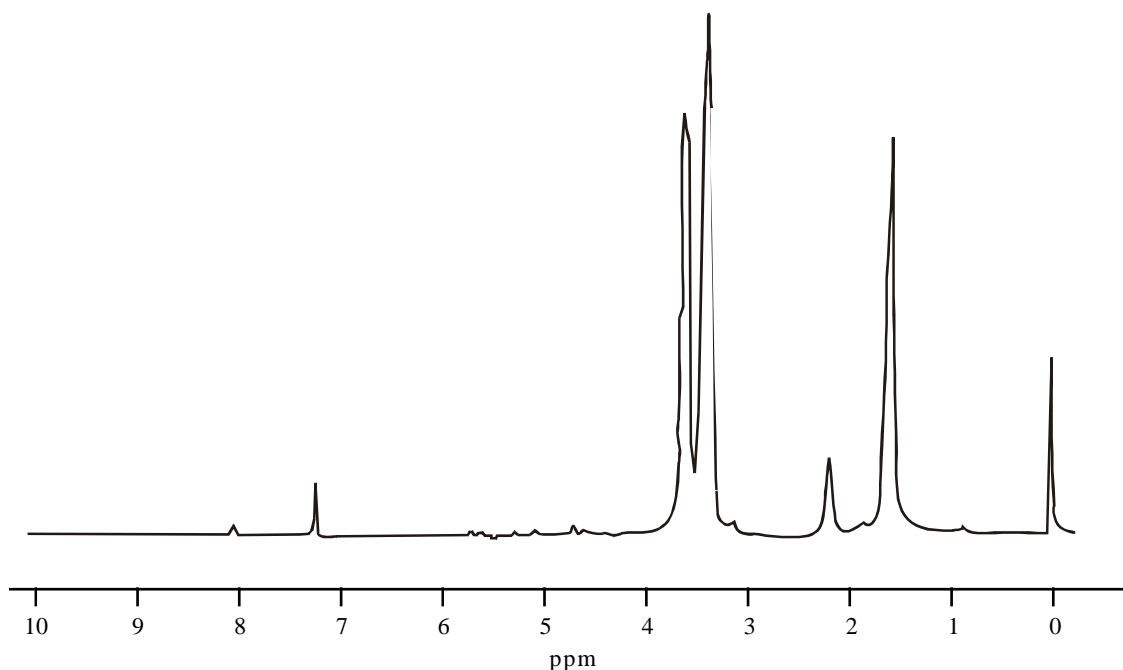
Figure 2. *^{1}H*-NMR of poly-BCMO-THF copolymer

crosslinks with HTPB and there is a considerable improvement in the tensile strength, as it was observed in the case of oligomeric phosphate ester[9]. But the improvement in tensile strength compared to the control (Table 2) is only marginal. This may be due to the insolubility of poly-BCMO in the HTPB matrix.

5.3 Flammability Test

The flammability of the samples containing poly-BCMO showed marginal rise in limiting oxygen

Table 2. Mechanical properties and limiting oxygen index of the cured samples

Formulation	Tensile strength (kgf/cm^2)	Elongation (%)	Limiting oxygen index (%)
HTPB	5.33	70.6	28.57
HTPB + 5 % Sb_2O_3	5.35	100.1	29.03
HTPB + 10 % Sb_2O_3	6.13	77.7	29.94
HTPB + 15 % Sb_2O_3	6.78	83.8	30.82
HTPB + 5 % Poly-BCMO	6.10	73.6	29.49
HTPB + 10 % Poly-BCMO	6.70	81.9	30.57
HTPB + 15 % Poly-BCMO	6.63	79.0	31.25

index. The limiting oxygen index, which is a measure of the flame retardancy, was found to be maximum with 15 per cent poly-BCMO-incorporated HTPB formulation as shown in Table 2. This is due to the presence of higher percentage of chlorine. The limiting oxygen index values of all the formulations are also given in Table 2.

5.4 Thermal Analysis

The DSC curve of BCMO showed an endothermic peak at 20 ºC corresponding to its melting. The DSC curves of poly-BCMO and BCMO-THF copolymer are shown in Figs 3 and 4, respectively. The DSC of poly-BCMO showed melting at 159 ºC, crystallisation at 152 ºC, and an exothermic decomposition with initiation of decomposition (T_i) at 330 ºC, and peak temperature (T_{max}) at 360 ºC. It showed a glass transition temperature (T_g) of 106 ºC. The DSC of BCMO–THF copolymer showed exothermic decomposition with T_{max} at 371 ºC and a T_g of – 30 ºC.

5.5 Thermogravemetric Analysis

The thermogravemetric curve of poly- BCMO is given in Fig. 5. It showed a single-stage decomposition with peak temperature (T_{max}) at 341ºC with an
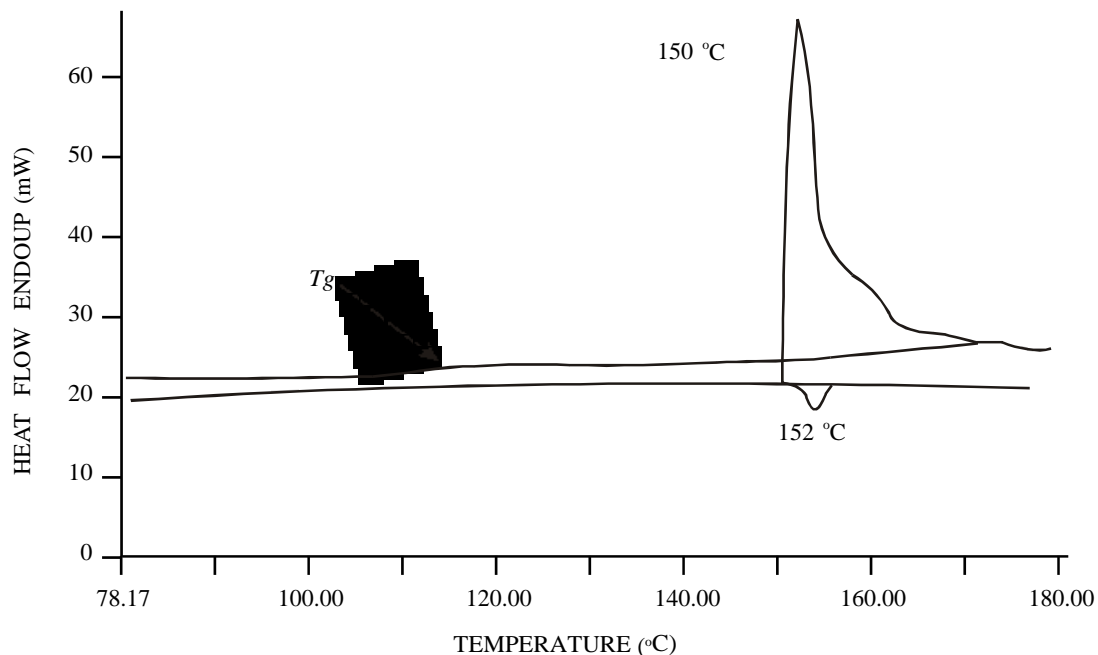
Figure 3. DSC of poly-BCMO

activation energy of 322 kJ/mol. The TGA curve of uncured HTPB showed two-stage decomposition with the first stage occurring in the temperature range 153–336 °C with T_{max} at 250 °C. This stage is accompanied by the weight loss of about 40 per cent. The second stage of decomposition was observed in the temperature range 339–579 °C

with a peak temperature of 460 °C accompanied with a weight loss of 58 per cent. The thermogravemetric results of cured HTPB with and without fillers indicate that there is no appreciable change in the thermal decomposition pattern and the T_{max} of the samples cured with toluene diisocyanate (TDI) and incorporated with
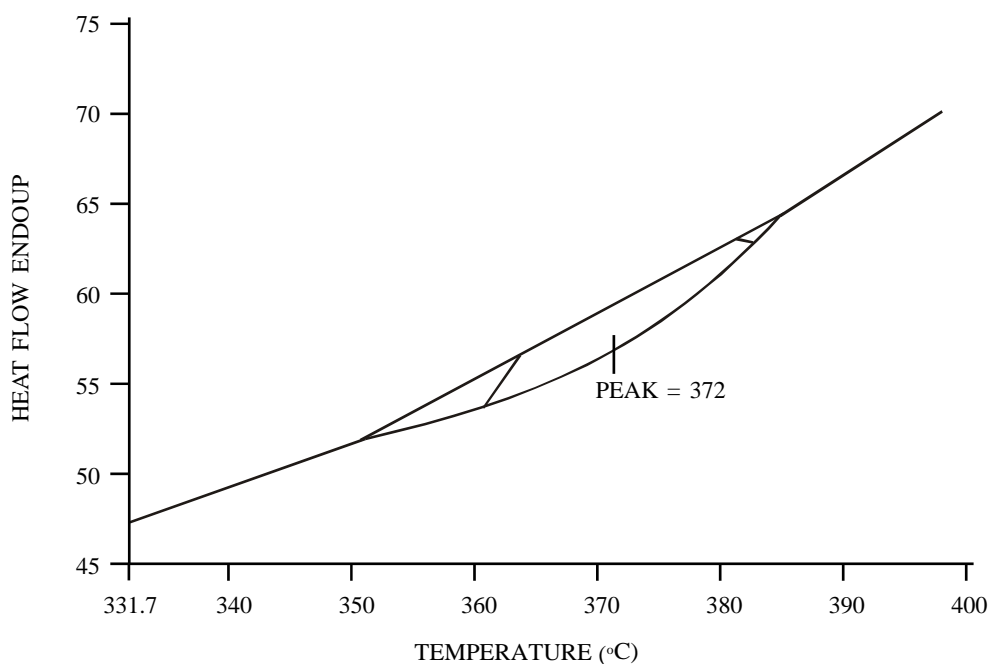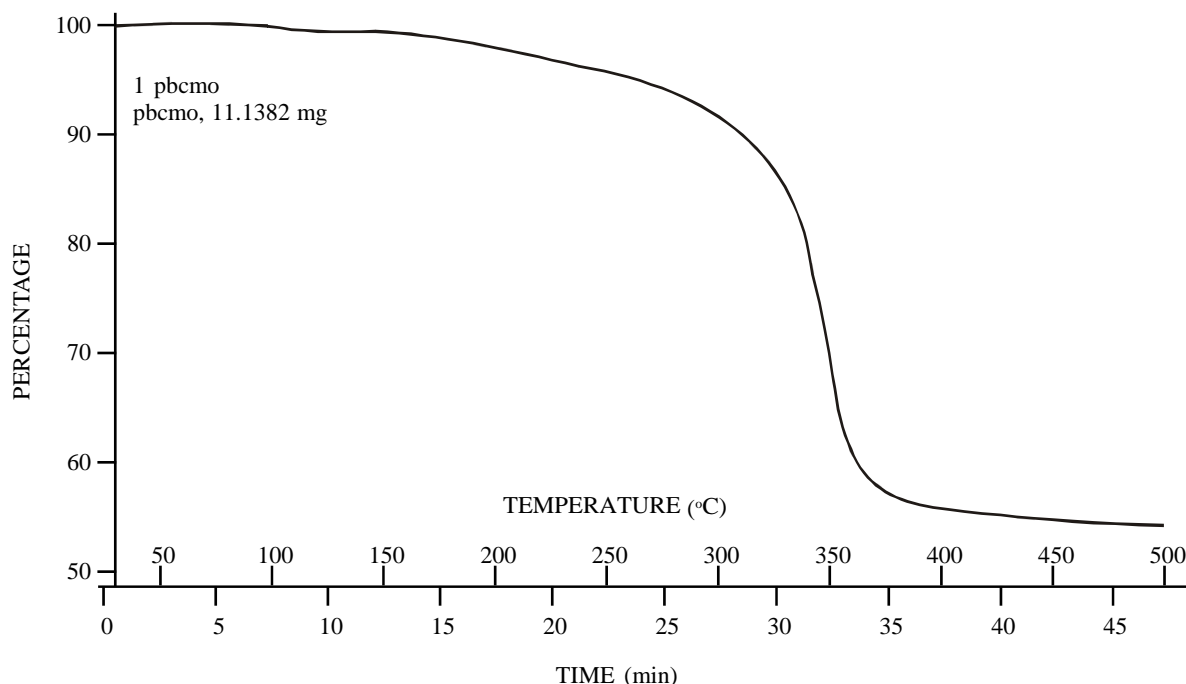

Figure 4. DSC of BCMO-THF

Figure 5. Thermogravemetric analysis of poly-BCMO

5 per cent, 10 per cent, and 15 per cent BCMO and Sb_2O_3.

5. CONCLUSIONS

BCMO, poly-BCMO, and BCMO-THF copolymer have been successfully synthesised in good yield and characterised satisfactorily. Flame retardancy of poly-BCMO has been investigated and it is found to be a better flame retardant than the currently used Sb_2O_3 for HTPB-based formulations. Poly-BCMO and BCMO-THF copolymer are precursors of poly-BAMO and BAMO-THF copolymer, which are futuristic potential energetic binders.

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Contributors

Shri T.S. Reddy has done his MSc in Polymer Science from S.K. University, Andhra Pradesh, in 1998. He has published three papers in national and international journals. Presently, he is working on synthesis of energetic polymeric binders.

Shri K. K. Jayakumar has done his BSc from Calicat University, Kerala, in 1995. He has published 1 paper in the international symposium. Presently he is working on synthesis of energetic polymeric binders.