

## Synthesis and Characterisation of Bis-azido Methyl Oxetane and its Polymer and Copolymer with Tetrahydrofuran

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### ABSTRACT

Bis-azido methyl oxetane (BAMO) was synthesised from pentaerythritol in two steps. Pentaerythritol was chlorinated to yield a mixture of mono, di, tri and tetra chloro compounds. The trichloro compound on ring closure gives bis-chloro methyl oxetane (BCMO). It was reacted with sodium azide in aqueous medium to obtain BAMO. The latter was polymerised using  $BF_3$  etherate catalyst and 1,4-butanediol initiator. Similarly, the BAMO-THF copolymer was also synthesised. All the monomers and polymers were characterised by IR,  $^1H$ -NMR,  $^{13}C$ -NMR, and refractive index. The polymers were also characterised for molecular weight, hydroxyl value, etc. Thermal analysis showed that both polymers degrade exothermically with  $T_{max}$  of 237 °C for polyBAMO and 241 °C for BAMO-THF copolymer with activation energy of 39 kcal/mol and 40 kcal/mol, respectively. Explosive properties like impact and friction sensitivity of BAMO and the other polymers were also determined.

**Keywords:** Recyclable binder systems, tetrahydrofuran, THF, BCMO, polyBAMO, energetic polymers, BAMO, synthesis, solid propellant binders, pyrotechnic binders, high energy materials, thermoplastic elastomers, bis-azido methyl oxetane, BAMO-THF copolymers, azido-oxetane-based polymers

### 1. INTRODUCTION

Energetic polymers for propellant, explosive or pyrotechnic binder applications is no longer an emerging field. However, the synthesis of these polymers and their development toward binder applications is still not, by and large, widely published. Hence the development of these materials remains a critical area in the field of high energy materials. Polymers and copolymers based on azido-oxetanes<sup>1</sup> or their derivatives are attracting considerable attention for potential application as solid propellant binders due to their controlled molecular weight, low polydispersity, low glass transition temperature, high energy and ease of handling. Added to this is the possibility of formulation of thermoplastic elastomers<sup>2</sup> using azido oxetanes, which offer high potential of developing recyclable

binder systems. 3,3-Bis-azido methyl oxetane (BAMO) is perhaps the most prominent among the class of azido oxetanes in terms of the number of polymers and copolymers reported thereof. With its symmetrical azido groups, it assumes special significance as a hard block repeat unit in thermoplastic elastomer copolymers. However, the homopolymer poly BAMO, though an energetic polymer, is a solid, and cannot be used directly for binder applications. Many copolymers of BAMO with non-energetic comonomers like tetrahydrofuran (THF) have been reported<sup>3</sup>. The BAMO-THF copolymer is an excellent candidate for binder applications with its energetic BAMO content coupled with the THF block, which affords good mechanical properties.

The paper describes the synthesis and characterisation of BCMO, BAMO, polyBAMO

and the BAMO-THF copolymer. All these have been characterised by spectroscopic methods and thermal analysis. The impact and friction sensitivity of the azido compounds have also been discussed.

## 2. EXPERIMENTAL PROCEDURE

### 2.1 Materials

Pentaerythritol (98 %, Qualigens), thionyl chloride (98 %, Thomas Baker),  $BF_3$  etherate (48 %, Fluka), sodium azide (98 %, SD Fine chemicals), 1,4-butanediol (99 %, Fluka) and sodium hydroxide (98 %, Qualigens) were used as obtained.

### 2.2 Methods of Synthesis

BAMO was synthesised in two steps, namely (i) synthesis of BCMO, and (ii) azidation of BCMO to yield BAMO (Scheme 1).

#### 2.2.1 Synthesis of BCMO

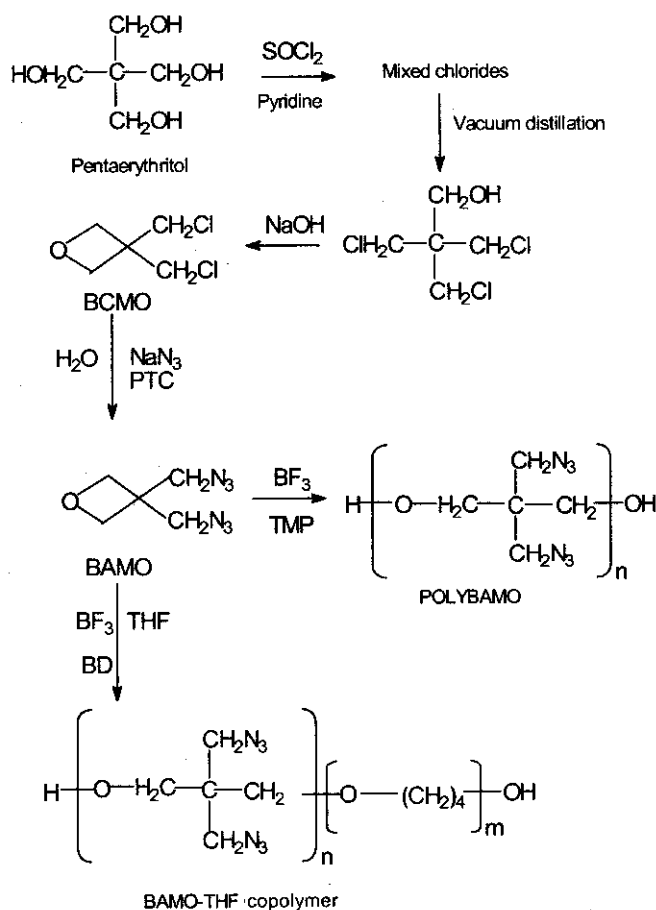
Pentaerythritol trichloride was prepared from pentaerythritol *via* chlorination using thionyl chloride followed by fractional distillation, according to the reported procedure. It was then cyclised according to the following method. Potassium hydroxide (1 mol) was dissolved in 98 per cent ethanol, pentaerythritol trichloride (1 mol) was added to it and the reaction mixture was refluxed for 15 min. Potassium chloride separated was filtered off and washed with ethanol. The combined filtrate and washings were concentrated and fractionated to yield BCMO<sup>4,5</sup>. Yield of BCMO was found to be 60 per cent, bp, 80 °C at 10 mm of Hg (trichloride, bp, 130 °C at 12 mm of Hg).

#### 2.2.2 Synthesis of BAMO

Sodium azide (0.195 mol) was taken in 50 per cent aqueous sodium hydroxide solution and BCMO (0.09 mol) was added to it, along with a small amount (0.0019 mol) of the phase transfer catalyst, tetraethylammonium bromide. The biphasic mixture was heated at 95–100 °C for 24 hr. The mixture was cooled, the organic layer was separated and washed with water and passed through a column packed with neutral alumina. Yield of BAMO<sup>6</sup> was found to be 88 per cent.

#### 2.2.3 Synthesis of PolyBAMO (Scheme 1)

Polymerisation of BAMO<sup>7</sup> was carried out using  $BF_3$  etherate as catalyst. 10 ml of dichloromethane, 16 moles of BAMO and 1 mole of trihydroxy methyl propane (TMP) were placed in a flask equipped with a mechanical stirrer and condenser attached to a guard tube containing calcium chloride. The catalyst,  $BF_3$  etherate (2 mol) was added and the reaction mixture stirred at room temperature for 6 hr. The polymerisation reaction was terminated by adding a few ml of ammonium hydroxide to destroy the catalyst complex. The solvent was evaporated under vacuum, the polymer washed with a small amount of methanol and dried under vacuum (mp, 76 °C). The polymerisation of BAMO was also carried out using 1,4-butane diol (BD) as an initiator.



Scheme 1: Syntheses of BCMO, BAMO, polyBAMO and BAMO-THF copolymer.

### 2.2.4 Synthesis of BAMO-THF Copolymer

The BAMO-THF copolymer<sup>3</sup> was prepared according to the reported method. THF (16 mol) was polymerised using  $BF_3$  etherate (4 mol) and 1,4-butane diol (2 mol) and the polymerisation was quenched by cooling the reaction mixture to  $-5\text{ }^\circ\text{C}$ . BAMO (16 mol) was then added to the above reaction mixture and stirred for 18 hr at room temperature. The polymerisation was terminated using sodium chloride solution equal to the volume of  $BF_3$  etherate used. It was subsequently washed with sodium bicarbonate and the contents were poured into methanol. The solvent was evaporated and the polymer was dried under vacuum.

The IR spectra were recorded on a Perkin-Elmer FTIR spectrophotometer model 1605 using smear technique. NMR spectra were recorded on a 300 MHz Bruker spectrometer, using TMS as internal standard and  $CDCl_3$  as solvent. Elemental analysis was carried out on a Perkin-Elmer elemental analyser model EA-1110. The DSC curves were recorded on a Perkin-Elmer DSC-7 instrument. The sample mass was  $\sim 2$  mg when heating rates of  $5\text{ }^\circ\text{C}/\text{min}$ ,  $10\text{ }^\circ\text{C}/\text{min}$ ,  $15\text{ }^\circ\text{C}/\text{min}$ ,  $20\text{ }^\circ\text{C}/\text{min}$  and  $25\text{ }^\circ\text{C}/\text{min}$  were employed. The TGA curves were recorded on a Mettler Toledo STAR<sup>e</sup> instrument in nitrogen atmosphere with a sample mass of  $\sim 10$  mg and heating rate of  $10\text{ }^\circ\text{C}/\text{min}$ . The impact sensitivity test was carried out on an impact sensitivity

apparatus of the fall hammer type with a falling weight of 2 kg. The friction sensitivity was measured using a Julius Peters friction sensitivity apparatus.

Number average molecular weight (Mn) was determined using a KNAUER vapour pressure osmometer. The hydroxyl value of the copolymer was determined. The copolymer was treated with 2 ml of standard acetylating agent (66 ml pyridine/33 ml acetic anhydride) for 15 min at  $95\text{ }^\circ\text{C}$ . Each analysis was then compared with a blank by titrating with 0.1 N sodium hydroxide. The difference in titrant between sample and blank was used to calculate the hydroxyl value of the copolymer.

### 3. RESULTS & DISCUSSION

BCMO has been synthesised by a tedious process in about 60 per cent yield and subsequently, BAMO, relatively easily in about 95 per cent yield. This two-step synthesis of BAMO affords an overall yield of 55-60 per cent. Both BCMO and BAMO have been found to be more than 98 per cent pure by HPLC. The characterisation data of BCMO and BAMO along with those of the polymers are given in Table 1, which also point to the high purity of the compounds synthesised.

The IR spectra of BCMO and BAMO are presented in Fig. 1. BCMO shows C-H,

Table 1. Characterisation of monomers and polymers

	BCMO	BAMO	polyBAMO	poly (BAMO-CO-THF)
IR ( $\text{cm}^{-1}$ )	1438 (oxetane) 1036 (C-O-C) 738 (C-Cl)	1446 C-H (oxetane) 1104 2102 ( $N_3$ )	2100 ( $N_3$ ) 3440 (OH)	2100 ( $N_3$ ) 3450 (OH)
(Mn)	—	—	2200	1900
DSC ( $^\circ\text{C}$ )	—	—	$T_i$ - 203 $T_m$ - 237	$T_i$ - 211 $T_m$ - 241
$T_g$ ( $^\circ\text{C}$ )	—	—	- 45	< - 50
OH(mg KOH/g)	—	—	81	63
n (25 $^\circ\text{C}$ )	1.4861 (1.4858)	1.5056 (1.5054)	—	—

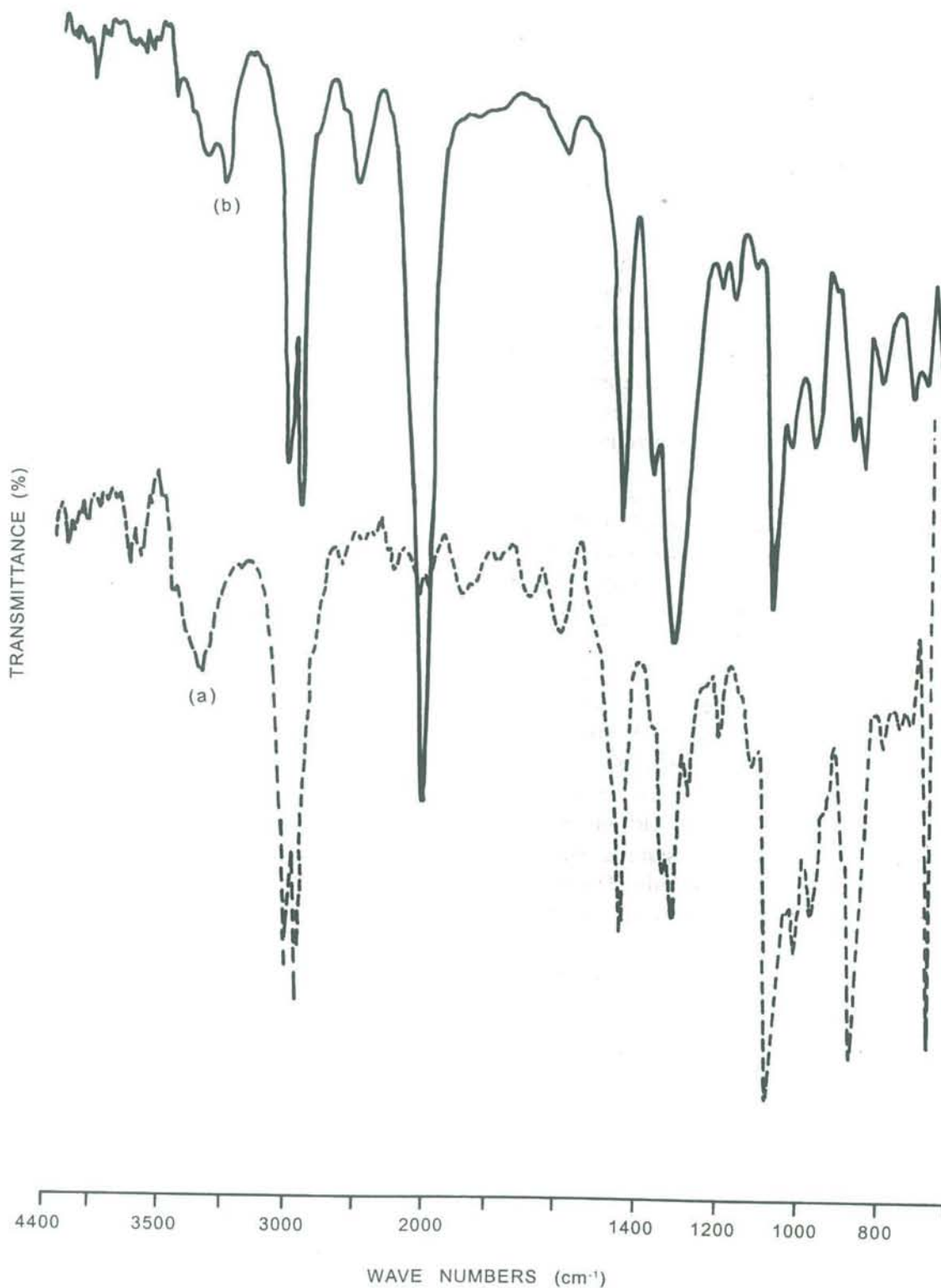


Figure 1. IR spectra of (a) BCMO and (b) BAMO

C-O-C and C-Cl stretching bands at 2962 cm<sup>-1</sup>, 1036 cm<sup>-1</sup>, and 738 cm<sup>-1</sup> and BAMO shows apart from the C-H and C-O-C stretching, the additional

band at 2102 cm<sup>-1</sup> due to the azide groups and it is devoid of C-Cl, evidenced by the disappearance of the band at 738 cm<sup>-1</sup>. Figure 2

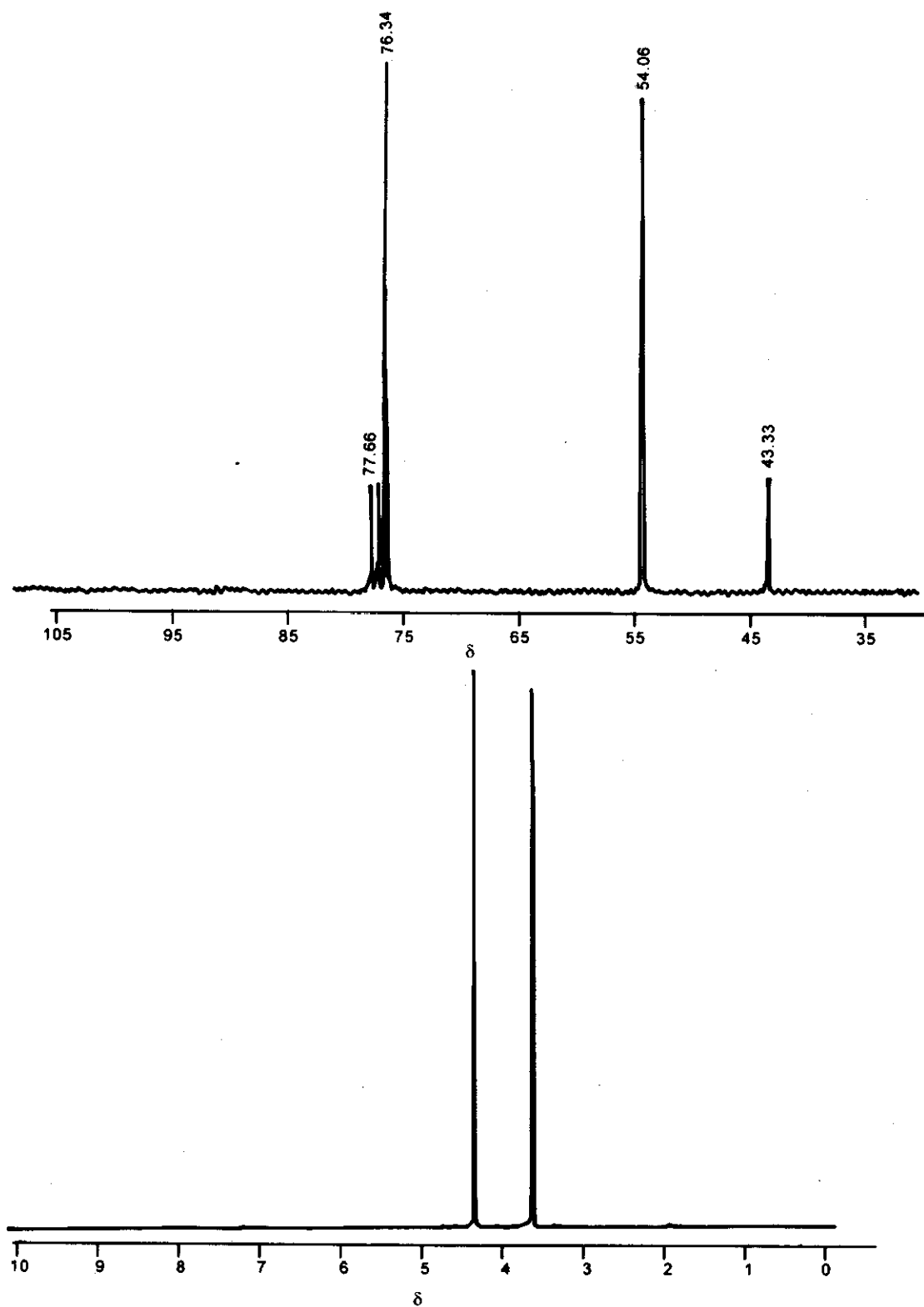


Figure 2.  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  spectra of BAMO

shows the  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  spectra of BAMO. The assignments are:  $^1\text{H-NMR}$ ,  $\delta$  3.66 (s, 4H,  $\text{CH}_2\text{N}_3$ ) and  $\delta$  4.37 (s, 4H,  $\text{OCH}_2$ ) and  $^{13}\text{C-NMR}$ ,

$\delta$  45.3 (bridge carbon),  $\delta$  54.06 ( $\text{CH}_2\text{N}_3$ ) and  $\delta$  76.36 ( $\text{OCH}_2$ ). Similarly,  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  of polyBAMO (Fig. 3) show a triplet at  $\delta$  0.85

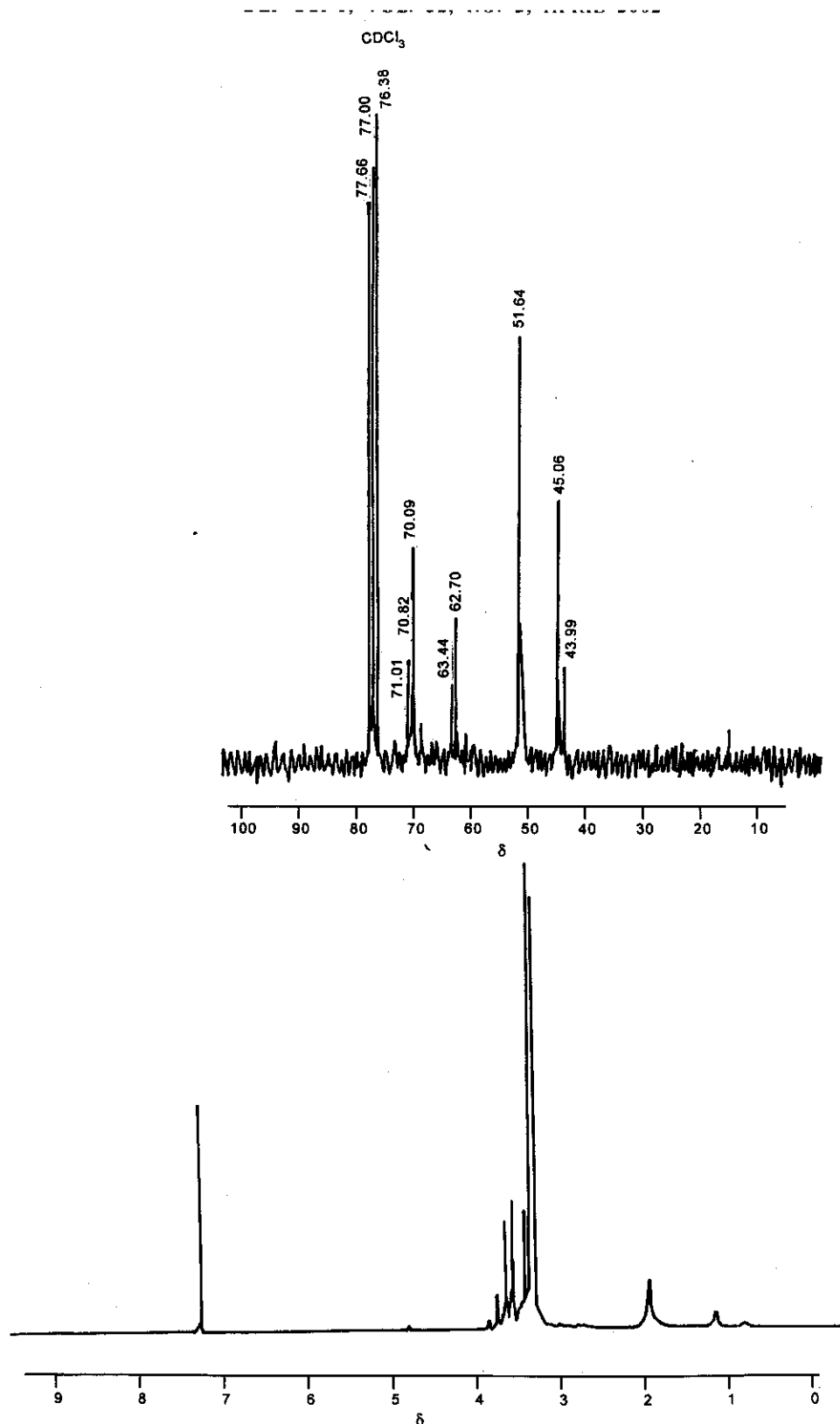


Figure 3.  $^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR spectra of polyBAMO

( $\text{CH}_2$  of TMP), a multiplet at  $\delta$  1.25 ( $\text{CH}_2$  of TMP), multiplet at  $\delta$  3.3 ( $\text{CH}_2\text{N}_3$ ) and multiplet at  $\delta$  3.6 ( $\text{CH}_2\text{O}$ ) and  $^{13}\text{C}$ -NMR spectra at  $\delta$  43.99 ( $\text{CH}_3$  of

TMP),  $\delta$  45.06 ( $\text{CH}_2$  of TMP),  $\delta$  51.64 (bridge carbon),  $\delta$  53.97 ( $\text{CH}_2\text{N}_3$ ),  $\delta$  62.70 ( $\text{CH}_2\text{OH}$  of TMP),  $\delta$  70.09 ( $\text{CH}_2\text{OH}$  of BAMO). The  $^1\text{H}$ -NMR

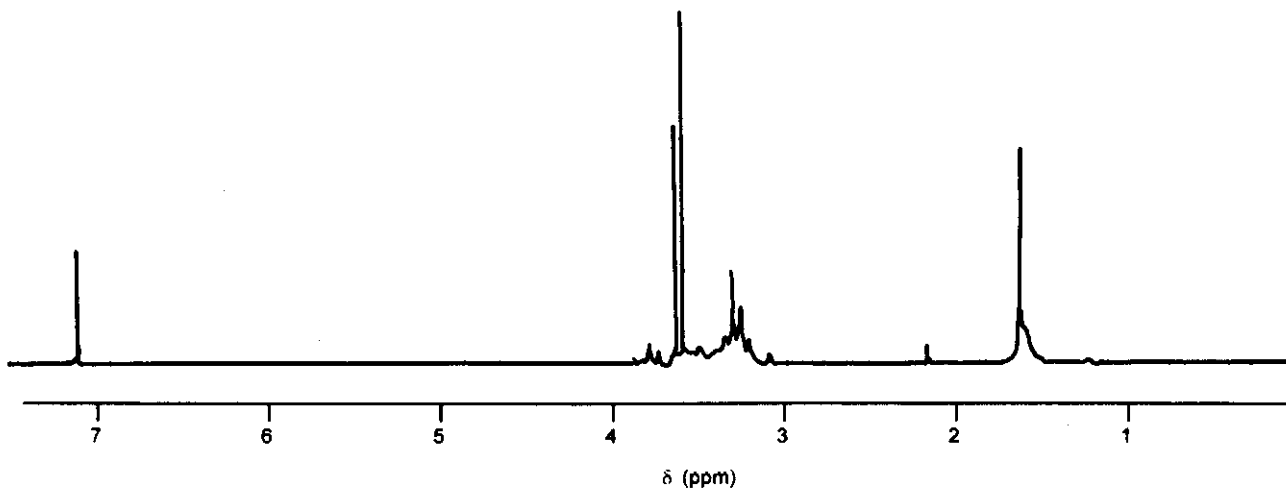
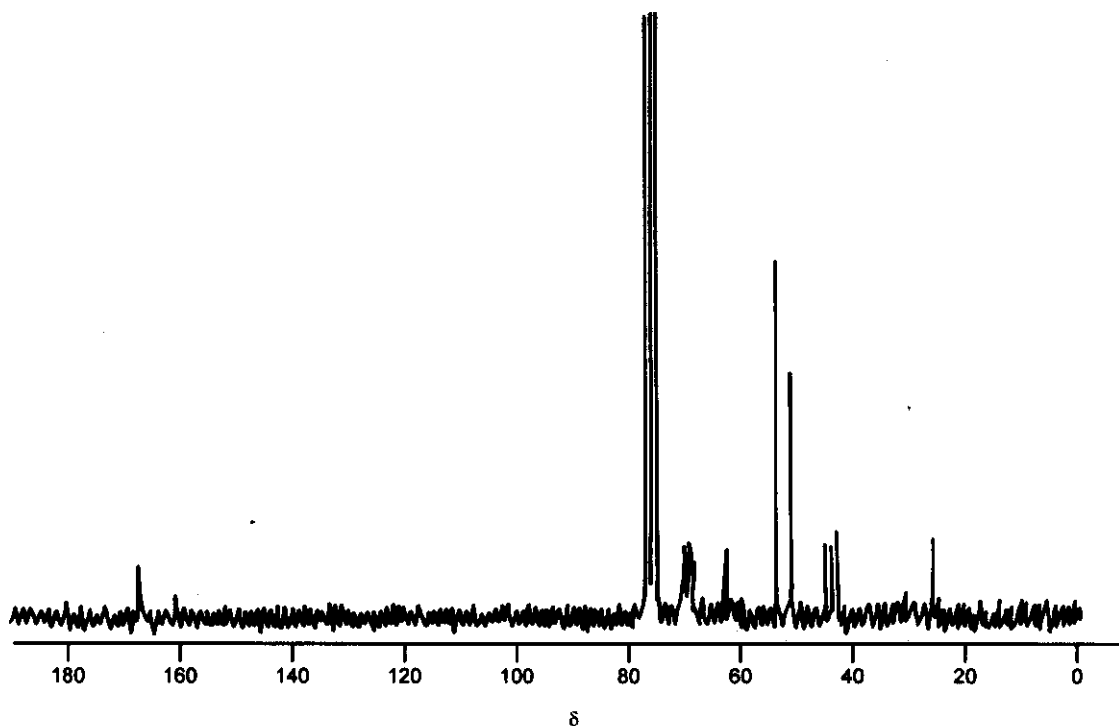


Figure 4. <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra of BAMO-THF copolymer

of BAMO-THF copolymer (Fig. 4) shows singlet at  $\delta$  1.68 ( $CH_2$  in THF), multiplet at  $\delta$  3.35 ( $CH_2N_3$ ) and multiplet at  $\delta$  3.65 ( $O-CH_2$  of THF as well as BAMO). <sup>13</sup>C-NMR spectra of copolymer (Fig. 4)

shows peaks at  $\delta$  26.00 ( $CH_2$  of BD),  $\delta$  44.89 ( $CH_2$  of THF),  $\delta$  51.55 (bridge carbon),  $\delta$  53.83 ( $CH_2N_3$ ),  $\delta$  62.36 ( $CH_2OH$  of BD), and  $\delta$  70.67 ( $CH_2OH$  of BAMO).

Table 3. Kinetic parameters of BAMO-THF copolymer

Heating rate (°C/min.)	$T_m$ (°C)	$T_m$ (K)	$1/T_m$ (K) <sup>-1</sup>	$T_m^2$	log $\beta$	ln $\beta$	Ln ( $\beta/T_m^2$ )
05	241.58	514.58	$1.94 \times 10^{-3}$	264796	0.70	1.61	-10.87
10	249.12	522.12	$1.92 \times 10^{-3}$	272609	1.00	2.30	-10.21
15	256.91	529.91	$1.89 \times 10^{-3}$	280808	1.18	2.71	-9.84
20	260.37	533.37	$1.87 \times 10^{-3}$	284486	1.30	2.99	-9.56
25	263.67	536.67	$1.86 \times 10^{-3}$	288015	1.39	3.22	-9.35

#### 4. CONCLUSIONS

The BCMO, BAMO, polyBAMO and the BAMO-THF copolymer have been successfully synthesised in good yields. All of these have been characterised well. BAMO, its polymer and copolymer were obtained in exceptionally pure forms.

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