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ATOM TRANSFER RADICAL POLYMERIZATION OF N-ISOPROPYL ACRYLAMIDE

AMBIKA SRIVASTAVA[1]

Department of Chemistry, Ramdayalu Singh College, Babasaheb Bhimrao Ambedkar Bihar University, Bihar, India

ABSTRACT

The polymerization of N-isopropyl acrylamide (NIPAM) under atom transfer radical polymerization (ATRP) conditions was studied. High monomer conversions were obtained using the initiator CIBB.

KEYWORDS: ATRP, N-isopropyl acrylamide, DSC

Research in living radical polymerization (Harrisson *et al.* 2025) has become an active area of polymer synthesis. Work has been published on nitroxide-mediated processes, (Truong *et al.* 2021) atom transfer radical polymerization (Matyjaszewski, 2024) and radical addition and fragmentation technique (Jeon*et al.* 2024). Most work on living radical polymerization has focused on styrene and methacrylates. Our particular interest in living radical polymerization has concentrated on the polymerization of acrylamide-based monomer (Antonopoulou *et al.* 2024). Polyacrylamides are an important class of water-soluble polymers, (Skanavis *et al.* 2024) and methods for controlled polymerization would be very valuable. Xie and Hogen-Esch (De Bon *et al.* 2024) have described the anionic polymerization of acrylamide monomers; these workers produced polyacrylamides with controlled molecular weight and narrow molecular weight distributions when polymerizations were conducted at low temperatures (78°C). The living free radical polymerization of acrylamides has not been widely studied. Recent reports have demonstrated controlled polymerizations using the nitroxide-mediated process (Benoit *et al.* 1999) and RAFT (Chong *et al.* 1999).

Therefore, these successful living polymerizations confirm that, compared to styrene and acrylate-based monomers, there is nothing intrinsically difficult about conducting living radical polymerizations of acrylamides. After considerable experimental effort, we have concluded that ATRP is an appropriate method for the living radical polymerizations of acrylamides.

MATERIALS

All reactions were carried out under purified nitrogen. Cu(I)Br (Aldrich 98%) was purified by successive washings with glacial acetic acid in order to remove any oxidized species, filtered, washed with absolute ethanol and diethyl ether, dried under vacuum and stored under purified nitrogen atmosphere. DMSO (Aldrich 98%) was used as the solvent. 2,2'-bipyridyl (99%) was used as the catalyst, and aluminum oxide(basic) was used as received from Aldrich. N-iospropyl acrylamide (NIPAM, Aldrich) was purified by vacuum distillation to remove stabilizer. Ligand N, N, N', N'', N'''- Penta methyl diethylenetriamine (PMDETA, Aldrich) was used as received.

Initiator Synthesis

In a 50ml round bottomed flask added 7-hydroxy 4-methyl coumarin (6mmol, 1056mg) and 10ml dry DMF and placed it in ice-bath. Then added NaH (12mmol, 276mg) in completely anhydrous conditions and stirred for 30 minutes. Then added 2-bromoisobutyryl bromide (12mmol, 1.5ml) and stirred at rt till the reaction completed as monitored by TLC. After the reaction evaporated the solvent, quenched with water to remove water soluble impurities and extracted with ethyl acetate. Then evaporated the organic extract to yield the crude solid. To obtain the pure product the solid obtained was chromatographed with ethyl acetate-hexane. White crystalline solid obtained. Yield: - 80%, m.p. 118°C. **^{1}H NMR (300MHz, DMSO-d_6):** 2.105(s,9H, $H^{f,}$ H^{b}), 6.472(s,1H, H^{a}), 7.270(d,1H, H^{d},J=8.7Hz), 7.350(s,1H, H^{e}), 7.923(d,1H, H^{c}). **^{13}C NMR (300MHz, DMSO-d_6):** 18.171, 29.956, 56.733, 109.570, 114.021, 117.614, 117.927, 126.655, 152.575, 152.814, 153.531, 159.465, 169.256. **FTIR (KBr, cm^{-1})** 3070(heteroaromatic –CH stretching), 1761(-C=O stretching of side chain ester), 1720(-C=O stretching of lactone), 1614,1466(aromatic C=C stretching), 1257(-C-O asymmetric stretching), 935(-C-O symmetric stretching), 576(C-Br stretching).

[1]Corresponding author

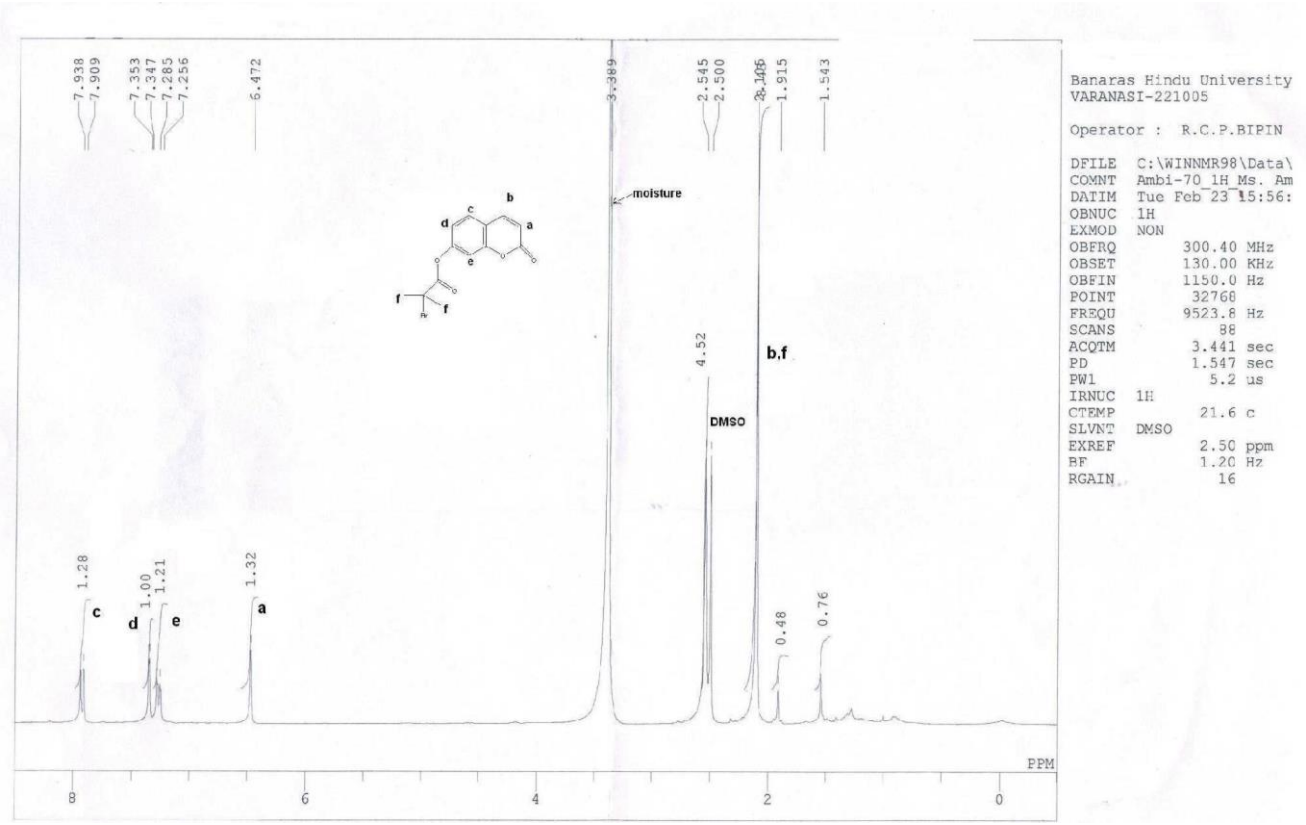


Figure 1: 1H NMR of initiator CIBB

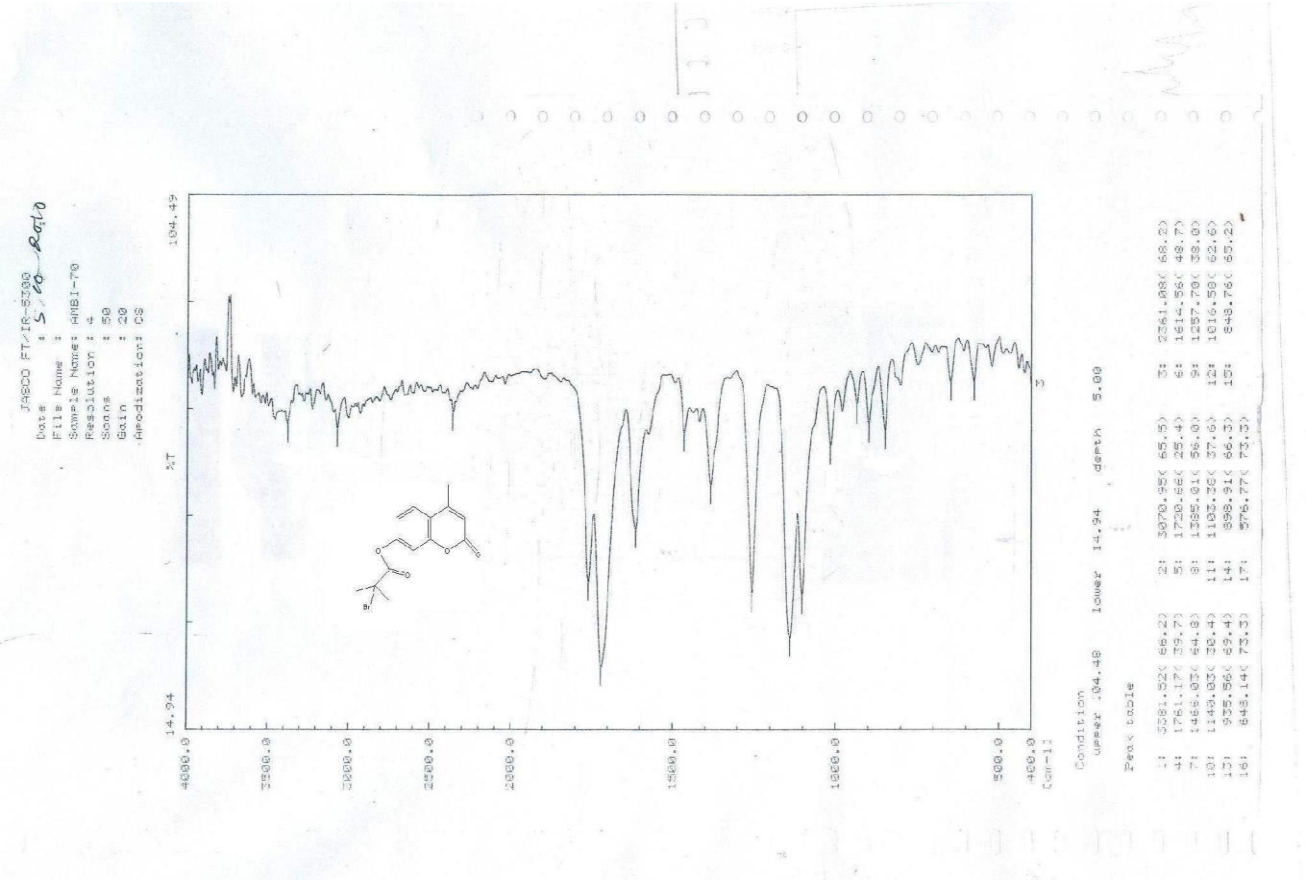


Figure 2: IR of initiator CIBB

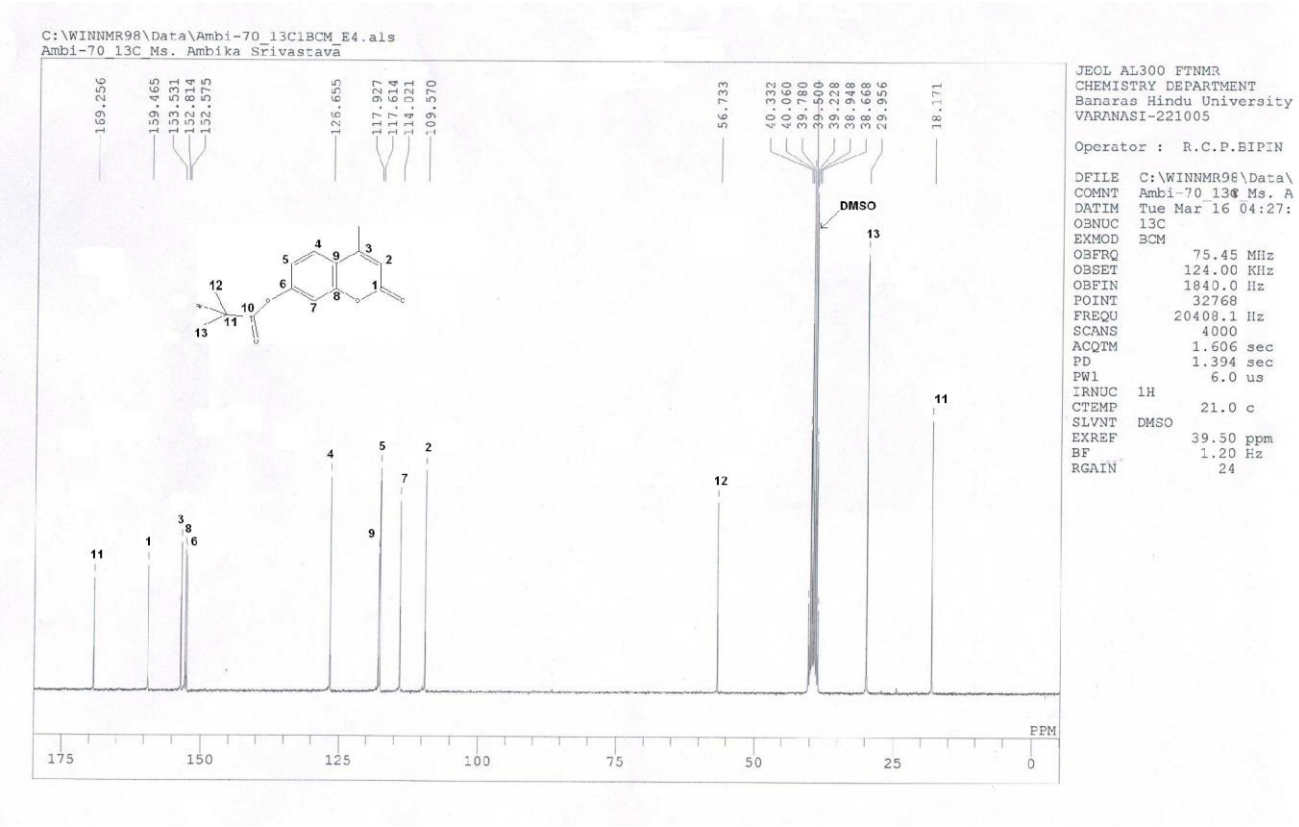
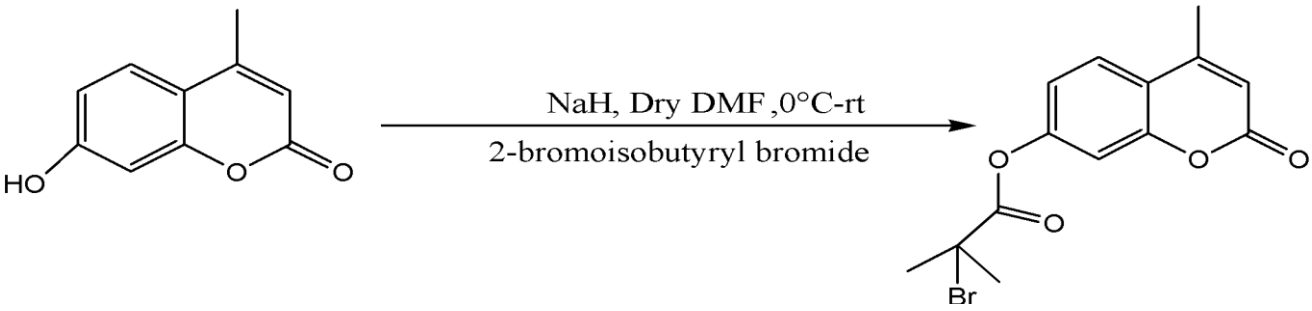


Figure 3: 13C NMR of the initiator CIBB

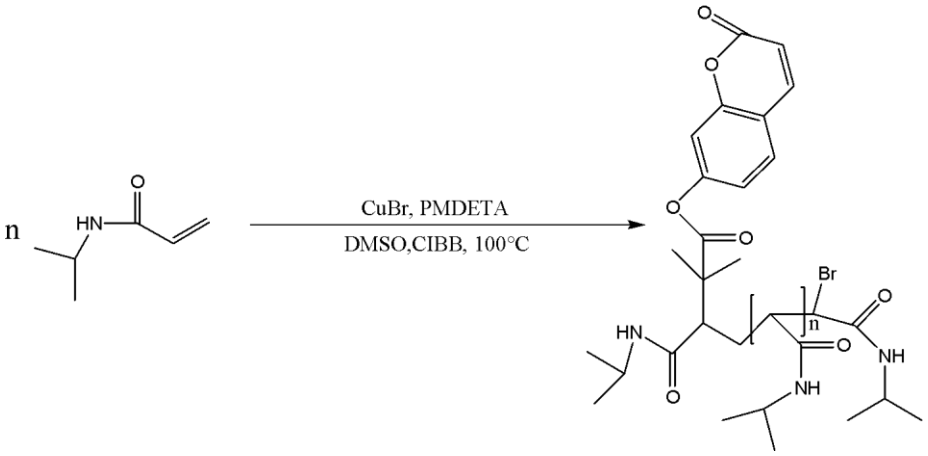


7-hydroxy-4-methyl coumarin Initiator (CIBB)

General Procedure for Polymerization

The ligand PMDETA (0.1mmol, 0.02ml) and dry DMSO (20ml) were first placed in a three neck round bottomed flask and the whole solution was purged with nitrogen. Three-freeze pump thaw cycle was performed to remove any trace of dissolved air or oxygen. Then added the deoxygenated monomer (NIPAM) (20mmol, 2.26g) and catalyst, copper (I) bromide (0.1 mmol, 9mg), again freeze pump thaw cycle was performed and finally flask was purged with nitrogen gas. The flask was then placed in an oil bath at 100°C and added the initiator CIBB (0.1mmol, 48.3mg). The polymerization was monitored at regular time intervals by ^{1}H NMR and % conversion is calculated. After a desired time, the reaction mixture was removed from the oil bath. Then extracted with diethyl ether 4-5 times to remove unreacted NIPAM and the dark green sticky residue left is dissolved in ethyl acetate. This solution is passed through basic alumina column to remove the copper catalyst and the filtrate was evaporated under reduced pressure. After 2 hours it became a hard solid, faded green in color. Yield: 335mg, **^{1}H NMR(300MHz, DMSO-d_6):** 1.150(broad,8H,$H^{a,e,f}$), 1.986(broad, 1H, H^{d}), 3.842(broad,1H,H^{b}), 7.174(broad,1H,H^{c}); **FTIR (KBr, cm^{-1}):** 3440(symmetrical N-H stretching), 2974(C-H stretching), 1648(C=O stretching), 1571,1461(C=C stretching), 1269(C-O stretching), 539(C-Br stretching).

Synthetic Pathway to Polymer Synthesis



MEASUREMENTS

NMR Measurements

NMR measurements were recorded at 300 MHz resonance frequency on a JEOL AL300 FT NMR at 23.2°C in DMSO-d_6 and $CDCl_3$ using trimethylsilane (TMS) as an internal reference.

FT-IR Measurement

FT-IR measurements were recorded on a Varian Excalibur 3000(Palo Alto, CA) spectrophotometer in the region 4000-400 cm^{-1} on KBr disc.

Electron Absorption Spectra

The electronic absorption spectra were recorded on PerkinElmer-Lambda 35. UV-VIS Spectrophotometer connected with PTP-1 Peltier system at 25°C. The optical path length of measurement cell was 10 mm.

Molecular Weight Distribution

All the molecular weights (Mw and Mn) and molar mass distribution (ĐM) of polymer samples were characterized at 40°C on a polymer laboratories PL GPC-220 with THF as eluent, at a flow rate of 1.0ml/min. Molecular weights were calculated using monodisperse poly (MMA) and polystyrene standards. Before injection into the GPC system, the polymer solutions were treated with cation-exchange resin Dowex 50W (Fluka) to free them from Cu salts. They were then filtered through a prefilter-filter combination system compatible with aqueous solutions.

Differential Scanning Calorimetry (DSC)

Glass transition temperature (T_g) of the products was measured on a Make/Model Mettler Toledo DSC 822e apparatus at a heating rate of 10°C/min. from -60°C to 350°C.

Differential Thermal Analysis (TGA)

Differential thermal analysis was carried out on a Make/Model Perkin Elmer, Diamond TG/DTA instrument with a heating rate of 80ml/min. in the nitrogen flow.

Scanning Electron Microscopy (SEM)

Observations were conducted on a JSM-6390 instrument at an accelerating voltage of 25 kV.

Crystal Structure Determination and Refinement

Data for the structure of initiator CIBB was obtained at 293(2) on Bruker three-circle and Oxford Gemini diffractometers, respectively, equipped with SMART 6000 CCD software using graphite mono-chromated Mo Kα (k = 0.71073 A˚) radiation **(Table 7)**. The structures were solved by direct methods (SHELXS-97) and refined against all data by full matrix least-square on F^2 using anisotropic displacement parameters for all non-hydrogen atoms. The structure is a, all hydrogen atoms were included in the refinement at geometrically ideal position and refined with a riding model. The MERCURY and encipher 1.3 packages were used for molecular graphics. Molecular structures were generated by use of the ORTEP-3 for windows program[l]. Crystallographic data and refinement details for the structural analysis are summarized in Table- and selected bond lengths and bond angles are given in Tables-1 and 2.

Monomer and Polymer Characterization

Initiator and polymer were characterized by ^1H NMR and IR. Molecular weights were determined by mass spectrometry. Thermal characteristics were determined by TGA/DTA and DSC, surface morphology by SEM. Monomer conversion was determined by gravimetry. The content of the flask was first washed with

tetrahydrofuran (THF) and the polymer was precipitated using a large excess of methanol. The precipitated polymer was filtered through filter paper and dried up to constant mass. The relative amount of homo monomers incorporated into the homo polymer was estimated from the integrated area under the appropriate peak intensities. Molecular weights were obtained using gel permeation chromatography (Waters 590) operating at room temperature with a refractive index (RI) detector on-line with a multiangle laser light-scattering photometer system. THF was filtered and used as the eluent at a flow rate of 1.0 mL/min. Samples for the analysis were prepared as 0.5% solutions in THF and filtered through 0.45 mm filters prior to injection.

RESULTS AND DISCUSSION

The bromide terminated well-controlled poly NIPAM polymer was synthesized using ATRP process. The feed molar ratio of $[NIPAM]_0$: $[CIBB]_0$: $[CuBr]_0$: $[bpy]_0$ (40:1:1:2) was maintained in the mixture by adding NIPAM (20mmol, 2.26g), initiator CIBB (0.1mmol, 48.3mg), ligand PMDETA (0.1mmol,0.02ml) and catalyst (0.1 mmol, 9mg). This mixture was placed in a three-neck round bottomed flask containing 20 ml degassed DMSO and Teflon coated magnetic bar. The solution was purged with purified and dried nitrogen gas for 30 min. The deoxygenated solution was placed in a thermostatic bath at 110°C for the desired time. At different time intervals, samples were taken for estimation of % conversion, and ^{1}H NMR. After a desired time, the reaction mixture was removed from the oil bath. Then extracted with diethyl ether 4-5 times to remove unreacted NIPAM and the dark green sticky residue left, is dissolved in ethyl acetate. This solution is passed through basic alumina column to remove the copper catalyst and the filtrate was evaporated under reduced pressure. After 2 hours it became a hard solid, faded green in color, polymerization was confirmed by ^{1}H NMR analysis. **NMR, IR and Mass interpretation:** From the ^{1}H NMR spectra of NIPAM and polyNIPAM it can be seen that while the a,b,c protons are coming at almost the same position in monomer and polymer ie. at δ 1.150, 3.842, 7.174 whereas the allylic protons have their position changed. d and e protons appear upfield at δ 1.446-0.837, and f at δ1.986. Peak for two methyl groups of initiators also superimpose in the same region ie. at δ 1.446-0.837, that's why it could not be seen separately.

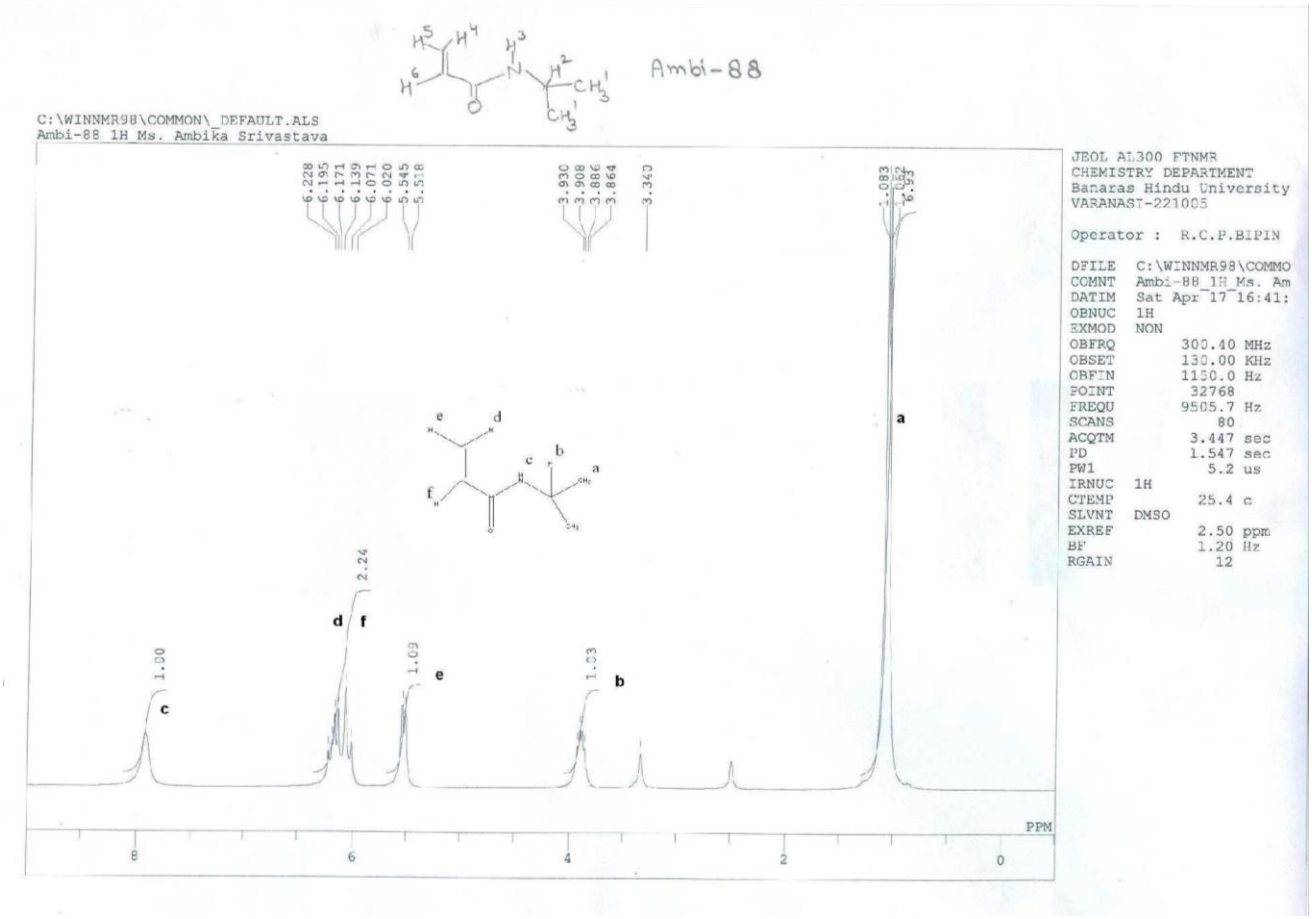


Figure 2: 1H NMR of NIPAM in DMSO-*d*6

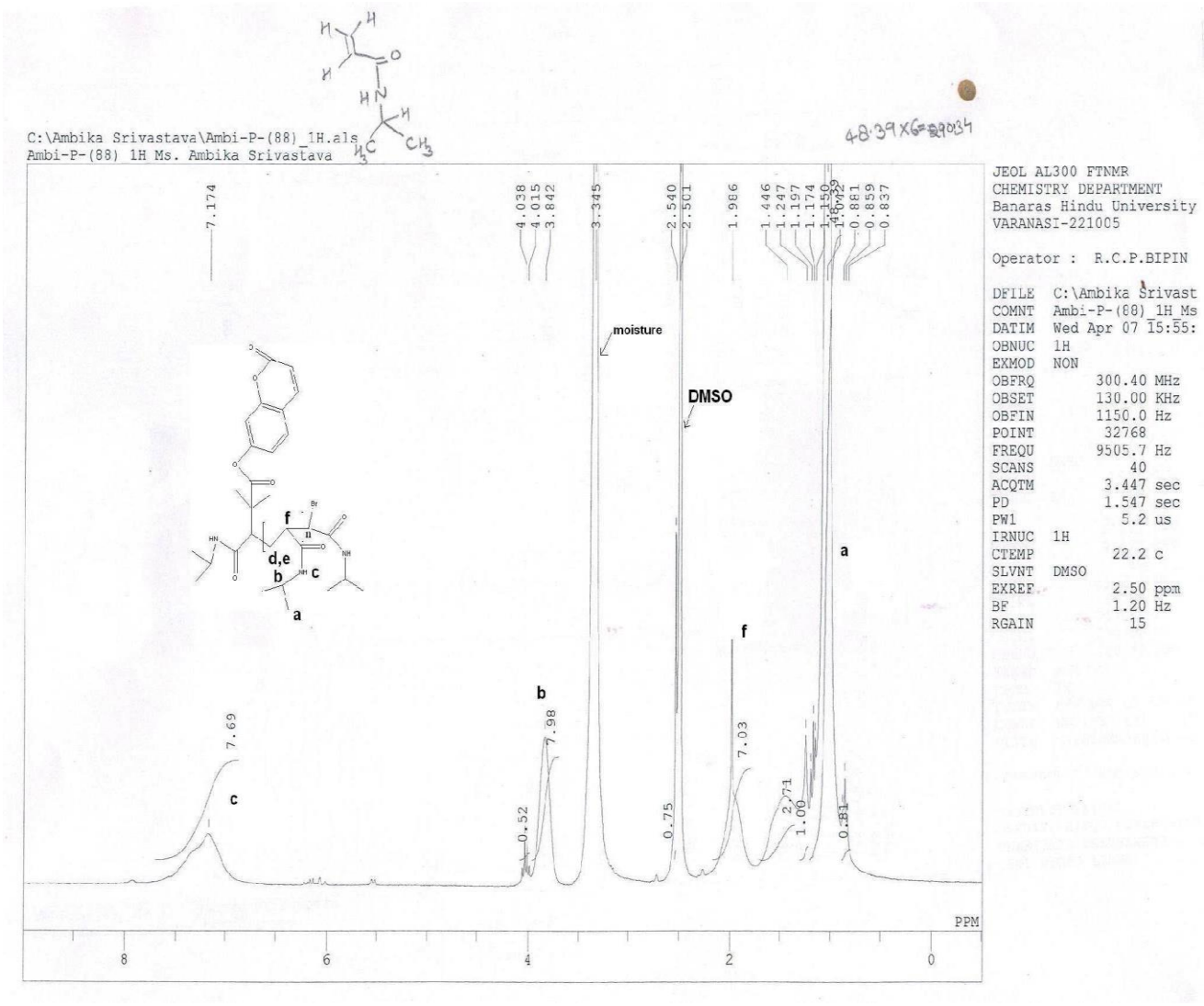


Figure 3: 1H NMR of poly NIPAM in DMSO-*d*6

Table 1: Crystallographic data and structure refinement for initiator CIBB

S.No.		
1.	Empirical Formula	$C_{14}H_{13}BrO_4$
2.	Formula weight	325.15
3.	T(K)	293(2)
4.	λ (Mo Kα)(Å)	0.71073
5.	Crystal system	
6.	Space group	P 2_1/n
7.	a (Å)	6.0517 (8)
8.	b (Å)	12.5973 (19)
9.	c (Å)	17.814 (3)
10.	α(˚)	90.00
11.	β(˚)	90.503(15)
12.	γ(˚)	90.00
13.	V (Å^3)	1358.0(3)
14.	Z	24
15.	ρ_{calcd} (mg/m^3)	
16.	μ(mm^{-1})	
17.	F(000)	3936
18.	Crystal size (mm^3)	
19.	θ range for data collection (˚)	3.23 – 28.67
20.	Index ranges	-5 ≤ h ≤ 7 -13 ≤ k ≤ 16 -23 ≤ l ≤ 17
21.	No. of reflections collected	3570
22.	No. of independent reflections	1341
23.	Number of data/restrains/parameters	1341/0/176
24.	Goodness-of-fit on F^2	0.855
25.	R_1^{α}, wR_2^{b} [I>2r(I)]	0.0840, 0.0422
26.	R_1^{α}, wR_2^{b} (all data)	0.1008, 0.0929
27.	Largest difference in peak and hole (e Å^{-3})	0.364, -0.420
28.	R-Factor (%)	4.22

Table 2: Bond lengths and bond angles have been demonstrated

S.No.	Atoms	Bond lengths	Atoms	Bond angles
1.	C11-Br	1.991(3)	C8-O1-C1	120.8(3)
2.	C8-O1	1.380(4)	O1-C8-C7	115.9(3)
3.	C1- O1	1.379(5)	C7-C8-C9	121.8(3)
4.	O4-C10	1.177(5)	O4-C10-C11	125.4(3)
5.	C14-C3	1.512(6)	C6-C5-C4	118.3(3)
6.	C8-C7	1.394(5)	C8-C7-C6	117.5(3)
7.	C011-C010	1.535(5)	O3-C6-C7	118.9(3)
8.	C6-C5	1.383(5)	C8-C9-C4	118.1(3)
9.	C5-C4	1.384(5)	C4-C9-C3	124.0(3)
10.	C4-C9	1.406(5)	C14-C3-C9	119.6(3)
11.	C9-C3	1.462(5)	C9-C3-C2	117.6(4)
12.	C3-C2	1.347(6)	O1-C1-C2	117.1(4)
13.	C1-C2	1.427(7)	C3-C2-C1	124.2(4)
14.	C13-C11	1.505(5)	Br-C11-C12	107.9(2)
15.	C7-C6	1.378(5)	C12-C11-C13	112.7(3)

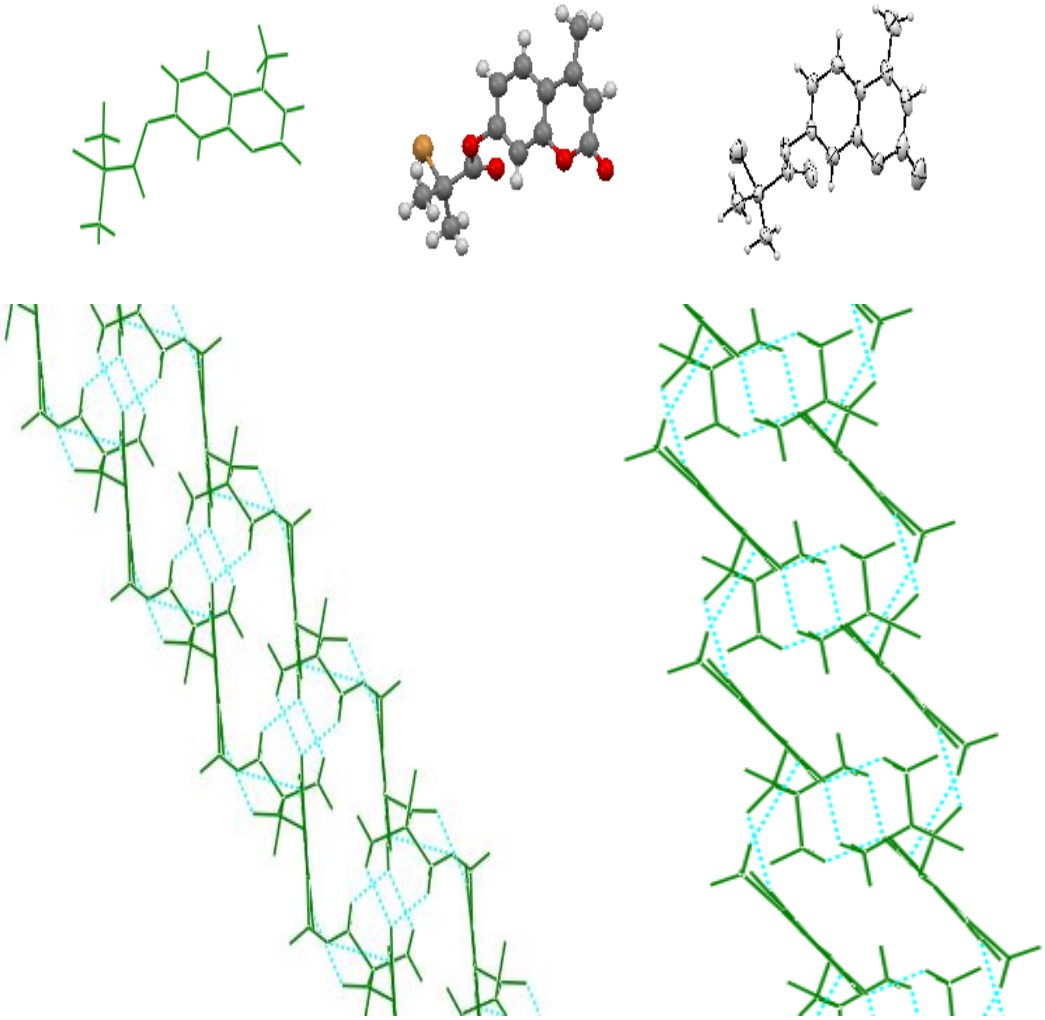


Figure 4: Wireframe, ORTEP, Publication structures of monomer and packing has been shown above

Different Formulae for Calculation of Parameters

1. Calculation of Conversion: The conversion of monomer to polymer was determined by ^{1}HNMR using the equation 1;

$$\%C_{NMR} = \frac{I_{Polymer}}{I_{Polymer} + I_{Monomer}} \times 100 \quad \text{Eq. (1)}$$

$$\%\,\text{Gravimetric conversion} = \frac{\text{Weight of polymer formed}}{\text{Weight of monomer in feed}} \times 100$$

Eq. (2)

2. Calculation of Number Average Molecular Weight:

$$Mn_{NMR} = M_{initiator} + M_{Monomer} \times \text{Degree of polymerization } (DP_n)$$

Eq. (3)

$$DPn = \frac{[Monomer]_0}{[Initiator]_0} \times Conversion \quad \text{Eq. (4)}$$

$$Mn_{Theo} = \frac{[\text{Monomer}]_0}{[\text{Initiator}]_0} \times Conversion_{Monomer} \times M_{Monomer} + M_{Initiator}$$

Eq. (5)

$$Mn_{UV} = \frac{w}{C_{Initiator}} \quad \text{Eq. (6)}$$

where, w, is the weight of polymer sample analyzed (in g), $C_{Initiator}$ is the amount of initiator residues in the polymer sample (in mol) determined experimentally by application of Beer's law and using the molar extinction coefficient of initiator. The absorbance of polymer was recorded and the concentration of initiator was calculated using the molar extinction coefficient of Initiator determined above.

$$\text{Initiator efficiency, } f = M_{n(THEO)} / M_{n(GPC)} \quad \text{Eq. (7)}$$

A semi-logarithmic plot of conversion *vs.* time gives the kinetic details of the polymerization. Linearity of the graph indicates the absence of termination reaction.

Y = m.x + c

$$\ln \frac{[M]_0}{[M]_t} = k_{aap}.t + c \quad \text{Eq. (12)}$$

and non-linear curve indicating the presence of side reactions. Here K_{app} is the ***apparent rate constant***.

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