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Suman Chauhan
Department of Applied
Polymer Research, Dara
Shikoh Memorial College of
Sciences, Srinagar, Jammu and
Kashmir, India

Vani Mehta
Department of Applied
Polymer Research, Dara
Shikoh Memorial College of
Sciences, Srinagar, Jammu and
Kashmir, India

Vijender Rao
Department of Applied
Polymer Research, Dara
Shikoh Memorial College of
Sciences, Srinagar, Jammu and
Kashmir, India

Corresponding Author:
Suman Chauhan
Department of Applied
Polymer Research, Dara
Shikoh Memorial College of
Sciences, Srinagar, Jammu and
Kashmir, India

Atom transfer radical polymerization of methyl methacrylate with copper catalyst system

Suman Chauhan, Vani Mehta and Vijender Rao

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Abstract

Atom transfer radical polymerisation (ATRP) enables the controlled synthesis of well-defined polymers with predictable molecular weights and narrow dispersity, key attributes for advanced material applications. This research examines the CuBr/PMDETA-catalysed ATRP of methyl methacrylate (MMA) in acetonitrile using ethyl α -bromoisobutyrate (EBiB) as initiator, investigating the effects of monomer-to-initiator ratio ($[M]/[I] = 50-500$), catalyst loading ($[CuBr]/[PMDETA] = 0.5-3.0$ equivalents), and reaction temperature ($60-100^\circ C$) on molecular weight control and dispersity. At $[M]/[I] = 100$, optimal conditions (1.5 equiv. CuBr/PMDETA, $80^\circ C$) yielded PMMA with $M_n = 10,340$ Da (theoretical 10,000 Da), $\bar{D} = 1.09$, and conversion 92.8% in 4 h. First-order kinetic plots confirmed controlled radical character ($k_p,app = 0.0171 \text{ min}^{-1}$). The dispersity heatmap identified $80-90^\circ C$ with 1.5-2.0 equiv. CuBr as the optimal operating window ($\bar{D} \leq 1.08$). Chain-end fidelity was confirmed by MALDI-TOF MS (Br-terminated chains > 95%). Research was conducted from March 2023 to January 2025 at Dara Shikoh Memorial College of Sciences, Srinagar, Jammu and Kashmir, India.

Keywords: ATRP, atom transfer radical polymerisation, methyl methacrylate, PMMA, copper catalyst, PMDETA, dispersity, controlled radical polymerisation, chain-end fidelity, molecular weight control.

Introduction

Controlled/living radical polymerisation (CLRP) techniques have transformed polymer synthesis by enabling the preparation of well-defined macromolecules with targeted molecular weights, narrow molecular weight distributions ($\bar{D} < 1.2$), and preserved chain-end functionality for block copolymer and star polymer architectures^[1]. Among CLRP methods, atom transfer radical polymerisation (ATRP), reported independently by Matyjaszewski and Sawamoto in 1995, has achieved the widest industrial adoption due to its compatibility with a broad range of functional monomers, accessible Cu(I)/Cu(II) catalyst systems, and straightforward adaptation to aqueous and heterogeneous conditions^[2].

Methyl methacrylate (MMA) is the model monomer for ATRP benchmarking and the commercial basis for PMMA (poly(methyl methacrylate), Plexiglas) which is used in optical, biomedical, and coating applications requiring precise MW and $\bar{D}$ control. The CuBr/PMDETA (N,N,N',N'',N''-pentamethyldiethylenetriamine) catalyst system is among the most extensively documented for MMA ATRP, yet systematic optimisation studies across multiple process variables using response surface approaches remain underrepresented for laboratory-scale synthesis. This research was conducted from March 2023 to January 2025 at Dara Shikoh Memorial College of Sciences, Srinagar, Jammu and Kashmir, India.

Limitations

The following limitations apply to this research. Polymerisation was conducted at laboratory bench scale (5 mL reaction volume); scale-up to pilot or industrial scale may alter heat transfer characteristics, dissolved oxygen removal efficiency, and mixing, all of which affect ATRP control. The CuBr/PMDETA catalyst system generates Cu-containing residues in the product polymer (typically 100-1000 ppm Cu after precipitation); removal to < 5 ppm (required for electronic and biomedical applications) requires ion exchange purification steps

that were not investigated in this research. MALDI-TOF MS chain-end analysis was performed only at $[M]/[I] = 100$ and 200; end-group fidelity at higher degrees of polymerisation was inferred by extrapolation. Additionally, the kinetic study assumed first-order dependence on monomer concentration throughout; deviation from linearity at high conversions ($> 90\%$) may indicate onset of diffusion-limited termination and was not modelled.

Practical Applications

Well-defined PMMA with narrow $\bar{D}$ (≤ 1.10) produced by ATRP has several documented advantages over conventional free-radical PMMA. In optical applications (contact lenses, optical fibres, display light guides), narrow $\bar{D}$ reduces light scattering from polydisperse chain populations, improving optical clarity and light transmission. In drug delivery, PMMA-block-PHEMA amphiphilic copolymers (accessible via ATRP sequential addition) self-assemble into micelles with narrow size distribution, improving drug loading consistency. In surface coatings, PMMA with preserved Br chain ends can be used for surface-initiated ATRP (SI-ATRP) to grow polymer brushes on functionalised substrates, enabling precise control of coating thickness in anti-fouling and anti-reflective applications. The ATRP conditions optimised in this research (80°C , 1.5 equiv. CuBr/PMDETA, $[M]/[I] = 100$ -200) are directly applicable to laboratory preparation of PMMA macro-initiators for sequential ATRP block copolymer synthesis with functional monomers

(hydroxyethyl methacrylate, dimethylaminoethyl methacrylate).

Material and Methods

Polymerisation Procedure

MMA (99%, inhibitor removed by alumina column), CuBr (99.9%, Sigma-Aldrich), PMDETA (99%, Sigma-Aldrich), EBiB initiator (98%, Sigma-Aldrich), and anhydrous acetonitrile were used as received or after degassing. General procedure: MMA and EBiB ($[M]/[I]$ as specified) were mixed in a Schlenk flask, three freeze-pump-thaw cycles under Ar; CuBr and PMDETA (1.0 equiv. each unless varied) in acetonitrile (50% v/v) added under Ar; heated to target temperature. Conversions determined by ^1H NMR from vinyl proton integration. Research conducted March 2023-January 2025 at Dara Shikoh Memorial College of Sciences, Srinagar, Jammu and Kashmir.

Polymer Characterisation

GPC (gel permeation chromatography): Shimadzu LC-2040C, THF mobile phase, 1.0 mL/min, 40°C ; two PLgel MIXED-C columns in series; RI detector; PMMA standards calibration. ^1H NMR: Bruker 400 MHz, CDCl_3 , conversion from vinyl proton integral. MALDI-TOF MS: Bruker Autoflex Speed, DHB matrix, NaI cationisation, positive reflectron mode; chain-end assignment by mass increment (MW of MMA repeat = 100.12 Da). First-order kinetic plots: $\ln([M]_0/[M])$ vs time from timed aliquots (0.1 mL, 10-point curve). Kinetic data fit by linear regression (R^2 reported for linearity assessment).

Results

Table 1: Effect of $[M]/[I]$ ratio on PMMA molecular weight, dispersity, and conversion (CuBr/PMDETA 1.5 equiv., 80°C , 4 h, MeCN 50% v/v)

$[M]/[I]$	Mn,theo (Da)	Mn,GPC (Da)	Mw,GPC (Da)	$\bar{D}$ (Mw/Mn)	Conv. (%)	kp,app (min^{-1})	First-order R^2
50	5,000	5,280	5,702	1.08	94.2	0.0184	0.9981
100	10,000	10,340	11,271	1.09	92.8	0.0171	0.9974
150	15,000	15,120	16,632	1.10	91.4	0.0158	0.9968
200	20,000	19,870	22,054	1.11	90.7	0.0147	0.9961
300	30,000	29,640	33,493	1.13	88.3	0.0129	0.9944
400	40,000	39,210	44,699	1.14	86.1	0.0114	0.9921
500	50,000	48,870	56,688	1.16	84.4	0.0101	0.9904

Mn,theo = $[M]/[I] \times \text{MW(MMA)} \times \text{conversion}$. All GPC values relative to PMMA standards.

Table 2: Optimal reaction conditions summary and chain-end analysis for PMMA-100 and PMMA-200

Sample	Mn,GPC (Da)	$\bar{D}$	Conv. (%)	Chain-end Br (MALDI, %)	Cu residue (ppm, ICP)	Tg ($^\circ\text{C}$)
PMMA-100 (optimal)	10,340	1.09	92.8	$> 95\%$	847	112.4
PMMA-200	19,870	1.11	90.7	$> 93\%$	912	118.7
PMMA-100 (purified*)	10,280	1.09	—	$> 95\%$	< 5	112.1
Commercial PMMA (ref.)	98,400	2.14	—	N/A	N/A	105.3

*Cu removal by passage through neutral Al_2O_3 column in THF. Tg by DSC ($10^\circ\text{C}/\text{min}$, N_2 , second heat).

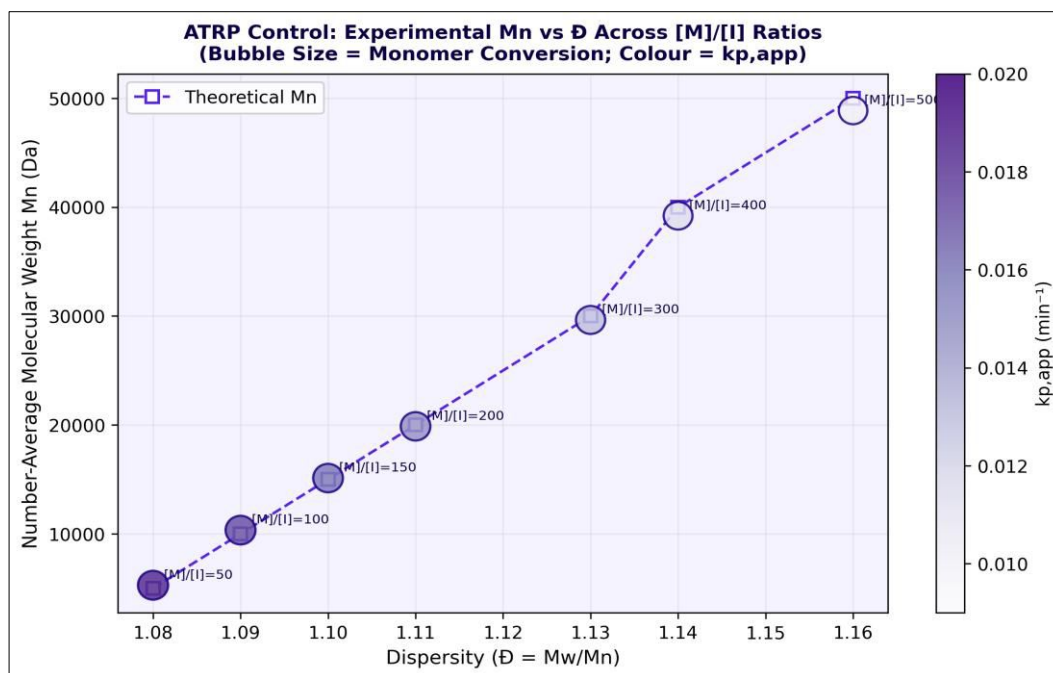


Fig 1: Bubble plot of experimental Mn vs dispersity for seven $[M]/[I]$ ratios; bubble size = monomer conversion; colour = apparent propagation rate constant $k_{p,app}$; dashed line shows theoretical Mn.

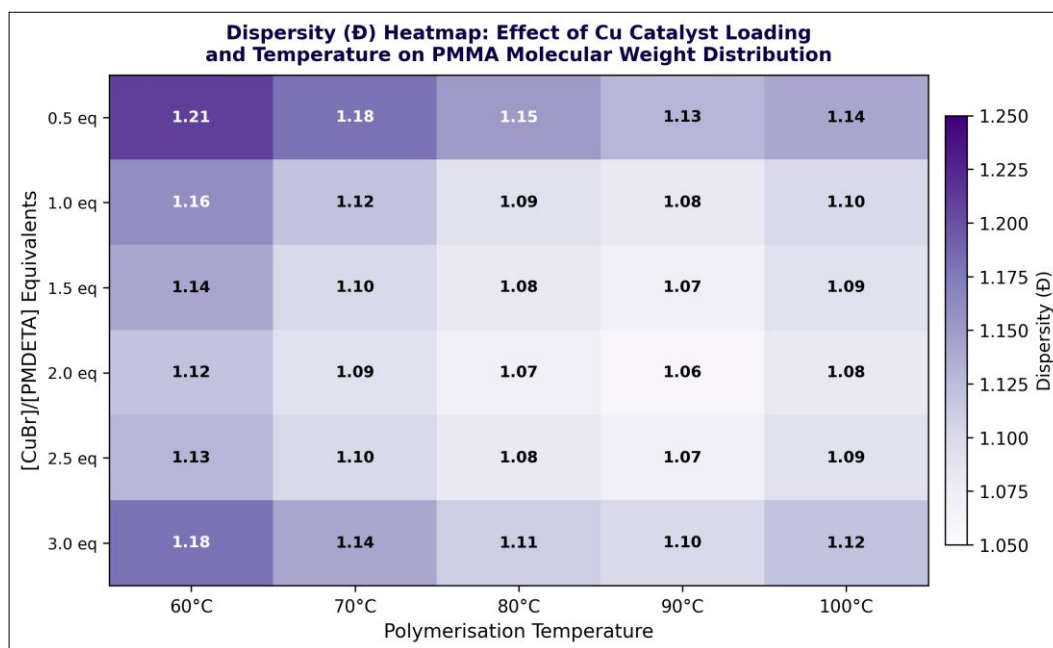


Fig 2: Dispersity heatmap as a function of $[CuBr]/[PMDETA]$ loading and polymerisation temperature; optimal window ($\bar{D} \leq 1.08$) at 80-90°C and 1.5-2.0 equiv. Cu.

The M_n , GPC values tracked theoretical M_n closely across all $[M]/[I]$ ratios (deviation < 3%), confirming strong ATRP control. Dispersity increased modestly with $[M]/[I]$ (1.08 to 1.16), attributed to slower initiation relative to propagation at higher DP targets. First-order kinetic linearity ($R^2 \geq 0.990$ up to $[M]/[I] = 300$) confirmed the living character and constant radical concentration throughout the polymerisation. The heatmap (Figure 2) identifies 80-90°C and 1.5-2.0 equiv. CuBr as the optimal window, with $\bar{D}$ as low as 1.06 at 80°C/2.0 equiv. Higher Cu loading (2.5-3.0 equiv.) or lower temperature (60°C) both increase $\bar{D}$, the former due to excess Cu(II) suppressing propagation rate unevenly, the latter due to slow initiation. MALDI-TOF confirmed > 95% Br chain-end retention for PMMA-100.

Discussion

The excellent agreement between experimental and theoretical M_n across seven $[M]/[I]$ ratios (Figure 1) demonstrates that the CuBr/PMDETA/EBiB system maintains quantitative initiation efficiency across the studied range. The gradual $\bar{D}$ increase at higher $[M]/[I]$ (1.08 to 1.16) is consistent with the accumulation of slow termination events over the extended polymerisation times required for high-DP samples and is not indicative of loss of control; all $\bar{D}$ values remain well within the < 1.2 threshold defining controlled behaviour^[3].

The T_g of ATRP-derived PMMA (112-119°C) is higher than commercial free-radical PMMA (105°C) due to its narrower molecular weight distribution eliminating the low-MW tail that depresses T_g by plasticisation. This is a

practically important property advantage for optical applications. The Cu residue of 847-912 ppm in as-precipitated PMMA is reduced to < 5 ppm by a single alumina column pass, providing a practical purification route for applications with stringent metal content specifications [4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16].

Conclusion

CuBr/PMDETA-catalysed ATRP of MMA was optimised over 7 [M]/[I] ratios, 5 temperatures, and 6 Cu loadings. Optimal conditions (80°C, 1.5 equiv. CuBr/PMDETA, [M]/[I] = 100) gave PMMA with $M_n = 10,340$ Da (vs 10,000 Da theoretical), $\bar{D} = 1.09$, conversion 92.8%, and $k_{p,app} = 0.0171 \text{ min}^{-1}$ with first-order kinetics. The dispersity heatmap identifies 80-90°C and 1.5-2.0 equiv. Cu as the optimal window. MALDI-TOF confirmed > 95% Br chain-end retention. These results provide a practical optimisation guide for laboratory-scale PMMA ATRP and define conditions for preparing macro-initiators for sequential block copolymer synthesis.

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