One-Pot Free Radical Polymerization of Block Copolymers via Thermal Activation of a Dual-Functional Initiator

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Abstract

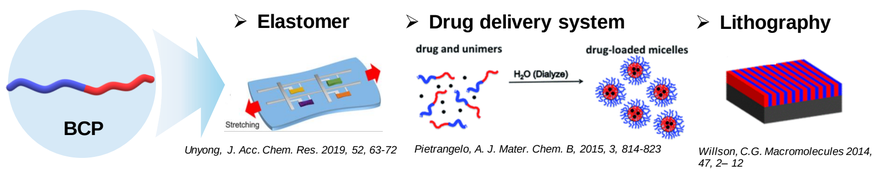
Dual-functional initiators that incorporate both azo and per-ester groups enable efficient block copolymer synthesis by allowing polymerization under varying conditions. Since the 1980s, azo-peroxide initiators have been utilized for block copolymer production through thermal, redox, and UV-induced initiation. [1] Previous studies relied on thermal initiation, redox activation, and UV irradiation. [2] While previous studies explored multiple activation mechanisms, our research introduces a more direct approach by exclusively utilizing thermal initiation. The proposed one-pot polymerization strategy eliminates the need for intermediate purification, streamlining the synthesis process compared to conventional methods.

In this work, we employ di-tert-butyl 4,4'-azobis(4-cyanoperoxyl-valerate) (AIBN-PEN) as a dual-functional initiator for thermal free radical polymerization (FRP). The polymerization process occurs in two stages: first, at 70°C, poly (methyl methacrylate) (PMMA) macro-initiators are generated; then, at 120°C, polystyrene (PSt) block growth proceeds. A semi-batch approach ensures balanced monomer consumption, stabilizing the overall polymerization kinetics. Soxhlet extraction is employed to remove residual homopolymers and other impurities, yielding high-purity PSt-b-PMMA. The formation of block copolymers is confirmed through gel permeation chromatography (GPC) and nuclear magnetic resonance (NMR) analysis.

Introduction

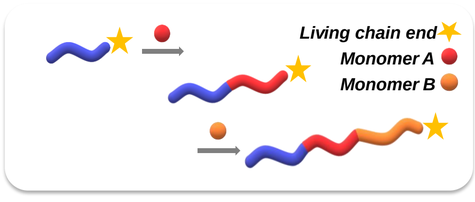
❖ Need for Free Radical Polymerization in Block copolymer Synthesis

❑ Applications of Block copolymer (BCP)



Unyong, J. Acc. Chem. Res. 2019, 52, 63-72
Pietrangelo, A. J. Mater. Chem. B, 2015, 3, 814-823
Willson, C.G. Macromolecules 2014, 47, 2– 12

❑ Conventional method for BCP synthesis



" *Living Polymerization* "

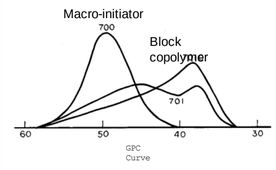
- Cationic polymerization
- Anionic polymerization
- Controlled radical polymerization ex) ATRP, RAFT, NMP

❑ Limit of living polymerization

***FRP* is better choice for commercialization**

❖ Our Research Concept

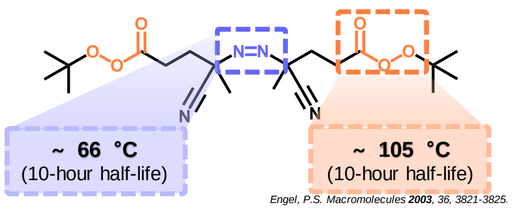
Previous Research



Piirma, I. J. Appl. Polym. Sci. 1979, 24, 2051–2070.

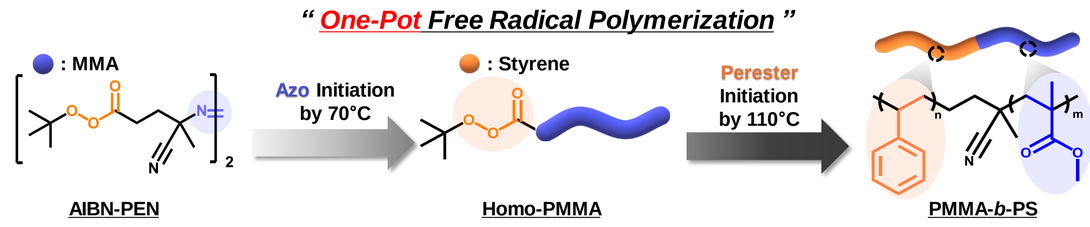
1st step : Perester activation by reducing agent at RT
↓ *purification*
2nd step : Azo activation by heat
↓
Formation of block copolymer

Azo-perester initiator (AIBN-PEN)



*Engel, P.S. Macromolecules **2003**, 36, 3821-3825.*

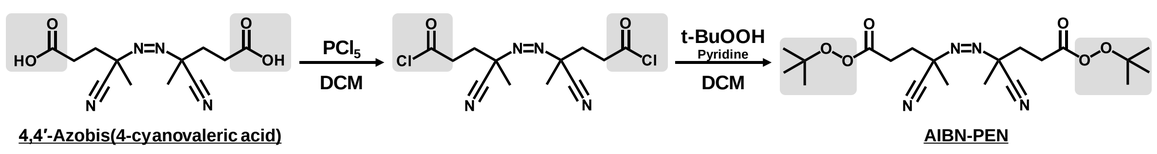
" *One-Pot* *Free Radical Polymerization* "



Result and Discussion

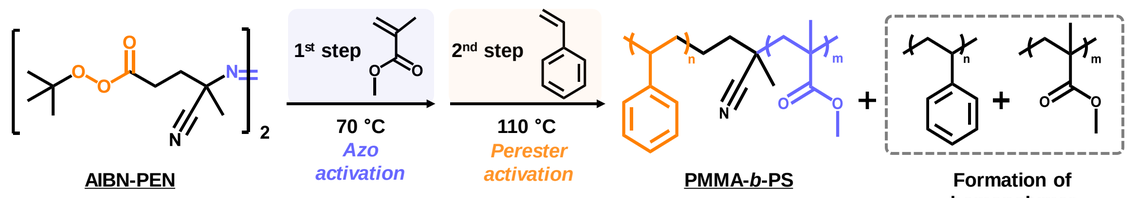
❖ Synthesis of BCP (Thermal-initiated)

❑ Scheme for synthesis of azo-perester initiator



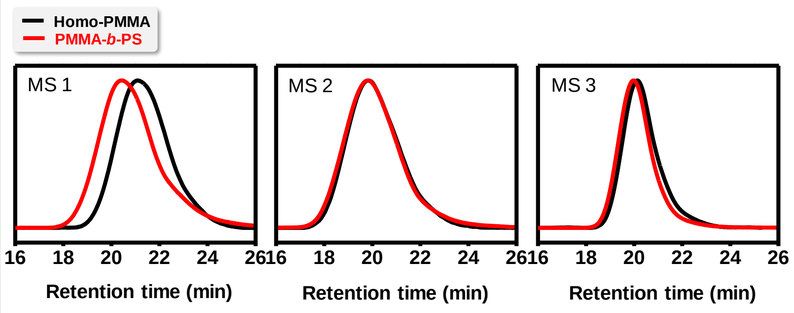
4,4'-Azobis(4-cyanovaleric acid) — AIBN-PEN

❑ Scheme for synthesis of PMMA-*b*-PS



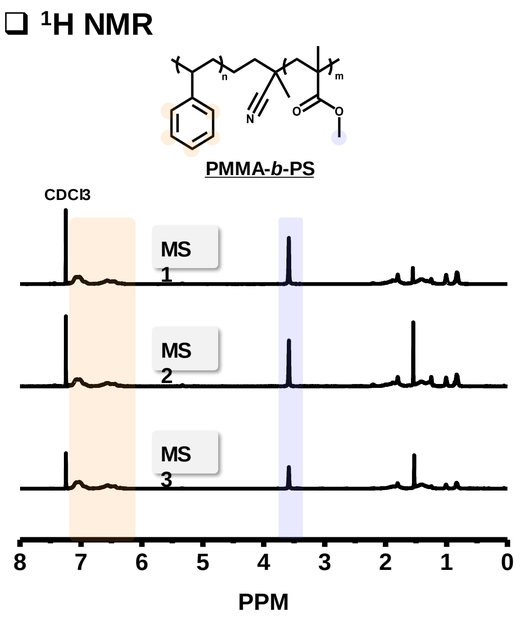
AIBN-PEN — PMMA-*b*-PS

❑ SEC



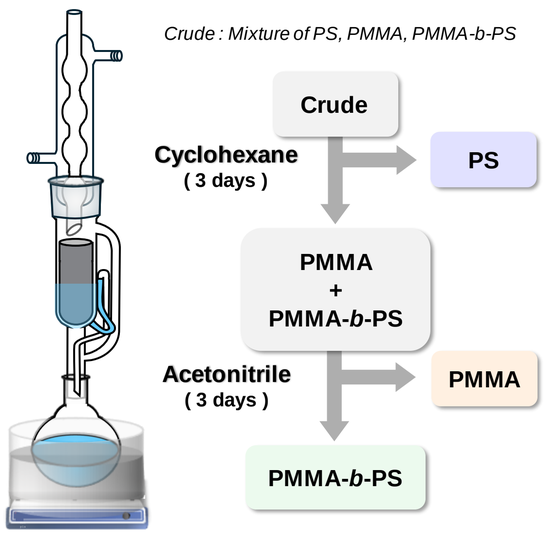
Sample	Homo-PMMA M_n (g/mol)	Homo-PMMA M_p (g/mol)	Homo-PMMA Đ	PMMA-*b*-PS M_n (g/mol)	PMMA-*b*-PS M_p (g/mol)	PMMA-*b*-PS Đ	Mol ratio PMMA : PS
MS 1	38,000	54,000	1.45	44,000	71,000	1.70	1 : 1.25
MS 2	75,000	111,000	1.57	78,000	113,000	1.66	1 : 1.34
MS 3	86,000	131,000	1.74	89,000	136,000	1.82	1 : 2.64

❑ ^{1}H NMR



❖ Soxhlet Extraction

❑ Extraction method

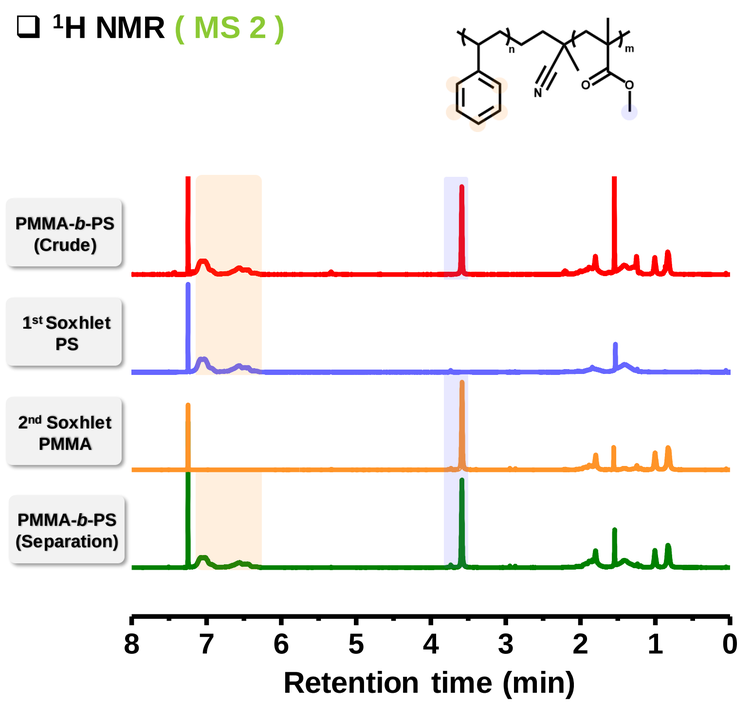


❑ Result of Separation

Sample	Block ratio (w/w) PS	PMMA	BCP
MS 1	40.3	15.3	44.3
MS 2	44.5	15.1	40.3
MS 3	59.5	18.8	21.8

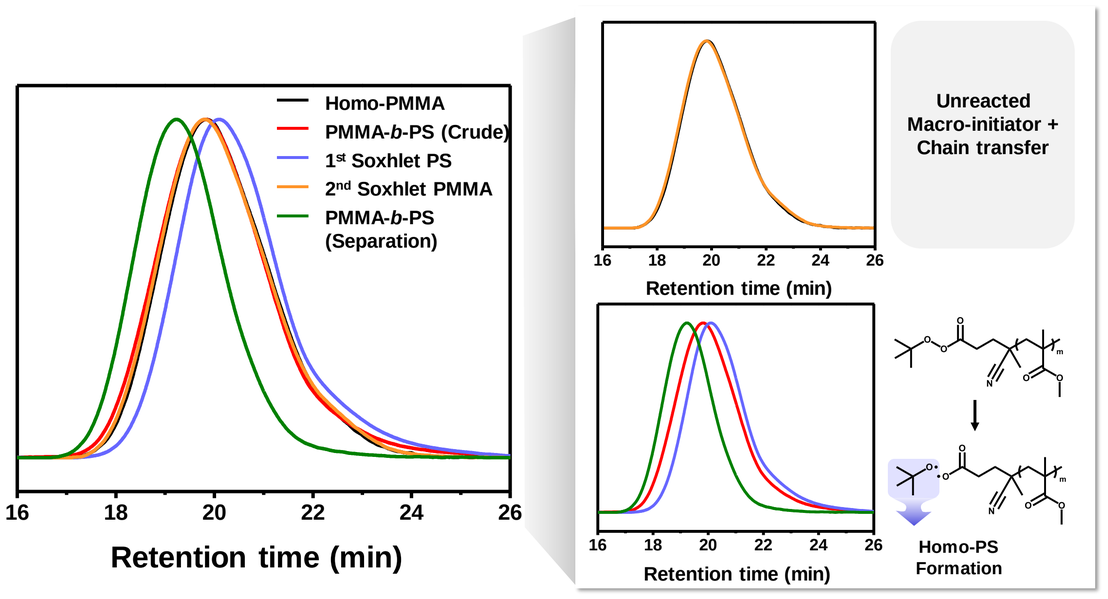
❖ Characterization of BCP after Separation

❑ ^{1}H NMR (MS 2)



Sample	Block ratio Before Soxhlet	Block ratio After Soxhlet
MS 1	PMMA : PS = 1 : 1.25	PMMA : PS = 1 : 1.17
MS 2	PMMA : PS = 1 : 1.34	PMMA : PS = 1 : 1
MS 3	PMMA : PS = 1 : 2.64	PMMA : PS = 1 : 1.38

❑ SEC (MS 2)



Sample (MS 2)	M_n (g/mol)	M_p (g/mol)	Đ
Homo-PMMA	75,000	111,000	1.57
PMMA-*b*-PS (Crude)	78,000	113,000	1.66
1st Soxhlet PS	46,000	76,000	1.70
2nd Soxhlet PMMA	70,000	108,000	1.62
PMMA-*b*-PS (Separation)	**130,000**	**161,000**	**1.43**

❖ BCP purity analysis

❑ RPLC (MS 2)

Sample	Area of reduced homo-polymer
PMMA	- 91%
PS	- 88%

Sample conc. : 0.5 mg / ml
Sample loading : 20 µL
Flow rate : 0.3 mL/min
Temp : 40 °C
Column : C18 silica column
(Lunasil C18, 4.6 × 150 mm, 5 µm, 100 Å)

Conclusion

- We successfully synthesized block copolymer via one-pot thermally-initiated free radical polymerization using a dual-functional initiator.
- Soxhlet extraction effectively removed residual homopolymers, improving the purity of the block copolymer.
- The synthesized BCPs were characterized using SEC, NMR, and HPLC, confirming successful block formation.
- We expect this method to be applicable to the synthesis of block copolymers for diverse functional applications.

Acknowledgement

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