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Atom transfer radical polymerization of 2-methoxy ethyl acrylate and its block copolymerization with acrylonitrile

A.S. Brar [*], Tripta Saini

Department of Chemistry, Indian Institute of Technology, New Delhi 110016, India

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Abstract

2-Methoxy ethyl acrylate (MEA), a functional monomer was homopolymerized using atom transfer radical polymerization (ATRP) technique with methyl 2-bromopropionate (MBP) as initiator and CuBr/*N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine (PMDETA) as catalyst system; polymerization was conducted in bulk at 60 °C and livingness was established by chain extension reaction. The kinetics as well as molecular weight distribution data indicated towards the controlled nature of polymerization. The initiator efficiency and the effect of initiator concentration on the rate of polymerization were investigated. The polymerization remained well-controlled even at low catalyst concentration of 10% relative to initiator. The influence of different solvents, viz. ethylene carbonate and toluene on the polymerization was investigated. End-group analysis for the determination of high degree of functionality of PMEA was determined with the help of $^{13}C\{^1H\}$ NMR spectra. Chain extension experiment was conducted with PMEA macroinitiator for ATRP of acrylonitrile (AN) in ethylene carbonate at 70 °C using CuCl/bpy as catalyst system. The composition of individual blocks in PMEA-*b*-PAN copolymers was determined using ^1H NMR spectra.

Keywords: Atom transfer radical polymerization (ATRP); Gel permeation chromatography (GPC); Kinetics; Molecular weight distribution

1. Introduction

The development of living radical polymerization for the synthesis of polymers with controlled architectures, molecular weight and narrow polydispersity is among the most significant accomplishments in polymer chemistry in the last decade. Of all the advances in living radical polymerization, atom transfer radical polymerization (ATRP) [1–5] has proved to have the potential for the direct application in the industrial production of polymers with controlled molecular weight distribution besides other controlled radical polymerization techniques such as reversible addition-fragmentation termination (RAFT) [6] and nitroxide mediated polymerization (NMP) [7]. Besides its usage for the controlled polymerization of acrylates [8–10], methacrylates [11–17], styrene [18–21], and acrylonitrile [22,23], the applicability of this technique has been explored to a great extent for the successful polymerization of wide range of monomers, viz. 1-octene [24],

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[*] Corresponding author. Tel.: +91 11 26591377.
E-mail address: asbrar@chemistry.iitd.ernet.in (A.S. Brar).

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3-ethyl-3-(acryloyloxy)methyloxetane [25], dimethyl-(1-ethoxycarbonyl) vinyl phosphate [26], allyl butyl ether [27], allyl methacrylate [28], potassium 2-sulfopropyl methacrylate [29], 5-methylene-2-phenyl-1,3-dioxolan-4-one [30], *N*-vinyl carbazole [31], 4-vinyl pyridine [32] etc.

The effect of variation of various reaction parameters on the kinetics as well as molecular weight distribution for the ATRP of various derivatives of acrylate monomers [33–40] have been investigated thoroughly. But, to the best of our knowledge, the ATRP of 2-methoxy ethyl acrylate (MEA) has not been investigated so far. The controlled polymerization of MEA is of immense importance since most of the industrial applications require well-defined products. Commercially, the polymers based on MEA are widely used as a coating material [41] to oxygenators due to their excellent blood compatibility. Block copolymers of acrylates and acrylonitrile are not only challenging synthetically, but also interesting because of the morphological and mechanical properties expected from these block copolymers. These properties are realized partly through the combination of a high glass transition temperature (T_g) block (acrylonitrile) with a softer, lower T_g block (acrylate). Moreover, these block copolymers are of interest since, after pyrolysis, they can result in well-organized nanostructure carbon materials [42]. There are only a few reports [43,44] on the synthesis of block copolymers containing polyacrylonitrile segments by ATRP. The synthesis of PMEA and block copolymers based on MEA with well-defined structure is of special importance for both their applications and the applicability of ATRP technique.

The present work describes the optimization of reaction conditions for the synthesis of PMEA (Scheme 1) of desired molecular weight with low polydispersity by ATRP. The effects of various reaction parameters viz. variation of initiator concentration, catalyst concentration, and solvent on the rate of polymerization were studied. An analysis of the end groups in PMEA was done with the aid of $^{13}C\{^1H\}$ NMR. Furthermore, block copolymerization with acrylonitrile (AN) was done using PMEA macroinitiators of different molecular weights. The purity of block copolymer was determined by gel permeation chromatography (GPC). The blocking efficiency of PMEA macroinitiators were investigated using the kinetics as well as molecular weight distribution data.

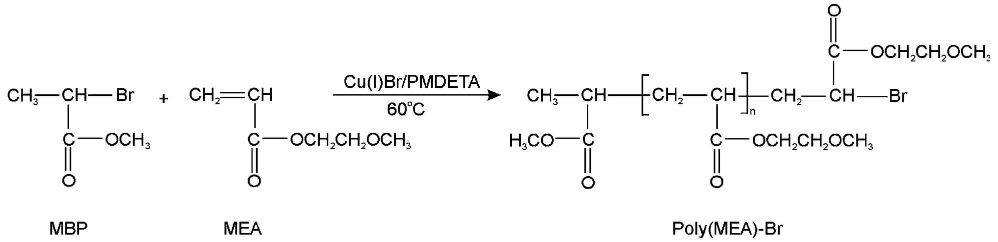
2. Experimental

2.1. Materials

2-Methoxy ethyl acrylate (MEA; 98%; Aldrich), acrylonitrile (AN; 99%; CDH) were passed through alumina column to remove inhibitor, vacuum distilled and kept below 5 °C prior to use. Methyl 2-bromopropionate (MBP; 98%; Aldrich), *N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine (PMDETA; 99%; Aldrich), ethylene carbonate (98%; Aldrich), CuBr (99.99%; Aldrich) and CuCl (97%; Aldrich) were used as received. 2,2′-Bipyridine (bpy, 99.5%, CDH) was recrystallized from acetone dried in vacuum before use.

2.2. Polymerization

All polymerization reactions were performed using standard Schlenck line techniques under a nitrogen atmosphere. In a typical procedure, calculated amounts of monomer (MEA) along with copper bromide (CuBr), and ligand (PMDETA) were added to the round bottom flask. The system was degassed by three vacuum-nitrogen cycles and stirred at the desired temperature for 10 min for the formation of catalyst. The calculated amount of purged initiator (MBP) was then added to the flask.



Scheme 1. Scheme for the homopolymerization of MEA in bulk at 60 °C using MBP as an initiator and CuBr/PMDETA as catalyst system.

The system was again degassed by three vacuum-nitrogen cycles and then sealed with septum. The flask was then placed in an oil bath maintained at 60 °C. The progress of the polymerization was monitored by the withdrawal of samples at timed intervals. The contents were then diluted with tetrahydrofuran (THF) and subsequently passed through a neutral alumina column to remove the catalyst. The excess THF was removed by rotary evaporation and the polymer was precipitated in large excess of methanol/water (1:1) system. The precipitated polymer was dried in a vacuum oven at 30 °C until constant weight was reached.

For block copolymerization reactions, in a round bottom flask, calculated amounts of monomer (AN), copper chloride (CuCl), and ligand (bpy) were taken along with ethylene carbonate. The calculated amount of purged macroinitiator of desired molecular weight was then added to the flask, which was then degassed by three vacuum-nitrogen cycles and then placed in an oil bath maintained at 70 °C. Samples were withdrawn at timed intervals to monitor the progress of the polymerization. The reaction mixture was then diluted with minimum amounts of *N*,*N*-dimethylformamide (DMF) and the polymer was precipitated in large excess of methanol/water (1:1) system. The solid polymers were dried in a vacuum oven at 30 °C until constant weight was reached.

2.3. Characterization

The monomer conversion was determined gravimetrically. Molecular weights were measured using gel permeation chromatography (GPC) equipped with a high pressure liquid chromatography pump (Bischoff) and a refractive index detector (Waters) against poly(methyl methacrylate) standards. The eluting solvent was dimethylacetamide (DMAc) with 0.12% LiCl at the flow rate of 0.5 ml/min at 80 °C. The end-group analysis was done using $^{13}C\{^{1}H\}$ NMR spectra. All the spectra were recorded on a Bruker DPX-300 NMR spectrometer in $CDCl_3$ at frequencies of 300.15 and 75.5 MHz for ^{1}H and ^{13}C, respectively, at 25 °C. For poly(2-methoxy ethyl acrylate-*block*-acrylonitrile), PMEA-*b*-PAN, all the spectra were recorded in deuterated dimethyl sulfoxide (DMSO-d_6) at 80 °C. The signal intensities of the spectra peaks were measured from the integrated peak areas calculated with an electronic integrator. NMR measurements were done on about 10% (w/v) polymer solutions.

3. Results and discussion

Based on the knowledge obtained from the available literature [1,2] on atom transfer radical polymerization (ATRP) of acrylate monomers, ATRP of 2-methoxy ethyl acrylate (MEA) was performed using methyl 2-bromopropionate (MBP) as initiator and CuBr/N,N,N',N',N''-pentamethyldiethylenetriamine (PMDETA) as catalyst. The initial polymerization was performed with molar ratio $[\mathrm{MEA}]_0$:$[\mathrm{MBP}]_0$:$[\mathrm{CuBr}]_0$:$[\mathrm{PMDETA}]_0 = 100{:}1{:}0.5{:}0.5$ in bulk at 60 °C. Typically, the reaction mixtures began as blue colored solutions due to the formation of active catalyst complex, which then changed to green during the polymerization reaction, indicating the formation of deactivating Cu(II) species.

The molecular weight data determined by gel permeation chromatography (GPC) for the ATRP of MEA with PMDETA as ligand is shown in Fig. 1. The number-average molecular weight (M_n) varied linearly with conversion with low polydispersity index (PDI), which indicates that the constant concentration of growing chains are present throughout the polymerization. Moreover, the evolution of molecular weight showed good agreement between the theoretical and experimental values. The theoretical number-average molecular weight ($M_{n,th}$) is defined as follows:

$$M_{n,th} = M_{w\ \mathrm{initiator}} + \left(M_{w\ \mathrm{monomer}} \times \frac{[\mathrm{monomer}]_0}{[\mathrm{initiator}]_0} \times \mathrm{conversion}\right)$$

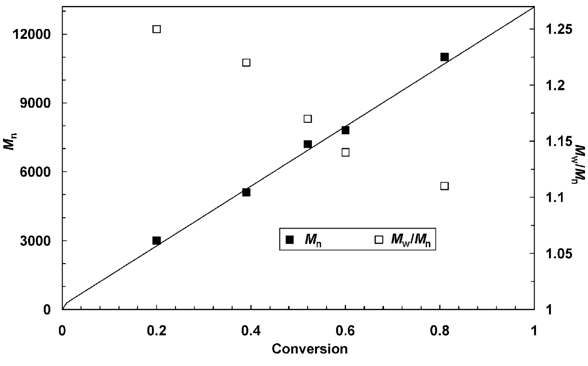


Fig. 1. Evolution of molecular weight and polydispersity as a function of conversion for the ATRP of MEA initiated by MBP and catalysed by CuBr/PMDETA ($[\mathrm{MEA}]_0 = 7.8$ M; $[\mathrm{MEA}]_0$:$[\mathrm{MBP}]_0$:$[\mathrm{CuBr}]_0$:$[\mathrm{PMDETA}]_0 = 100{:}1{:}0.5{:}0.5$). The solid lines represent the theoretical M_n values based on $[\mathrm{MEA}]_0$ and $[\mathrm{MBP}]_0$.

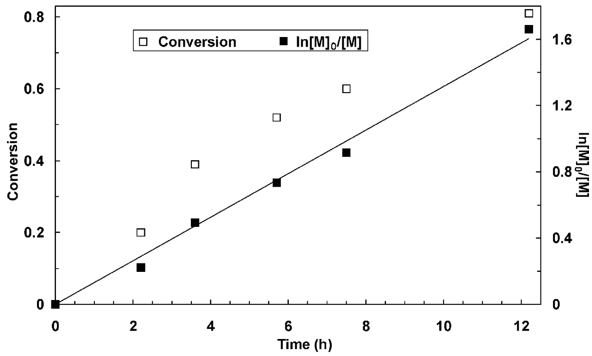


Fig. 2. Semilogarithimic kinetic plot for the ATRP of MEA in bulk at 60 °C with MBP as initiator and CuBr/PMDETA as catalyst system ($[\text{MEA}]_0 = 7.8$ M; $[\text{MEA}]_0:[\text{MBP}]_0:[\text{CuBr}]_0:[\text{PMDETA}]_0 = 100:1:0.5:0.5$).

where, $M_{\text{w initiator}}$ and $M_{\text{w monomer}}$ are the molar mass of initiator and monomer respectively, and $[\text{initiator}]_0$ and $[\text{monomer}]_0$ are the initial concentrations of the monomer and initiator, respectively. The first-order kinetic plot shown in Fig. 2 displayed linear relation with reaction time, further confirming the living nature of polymerization.

3.1. Effect of initiator concentration

Fig. 3 shows the kinetic plots of $\ln[M]_0/[M]$ versus time for the ATRP of MEA catalyzed by CuBr/PMDETA at three different concentrations of initiator (MBP). The polymerizations were approximately first-order with respect to the monomer, and the slopes indicate that the polymerization proceeded with an approximately constant number of active species present throughout the polymerization with negligible contribution of termination reaction.

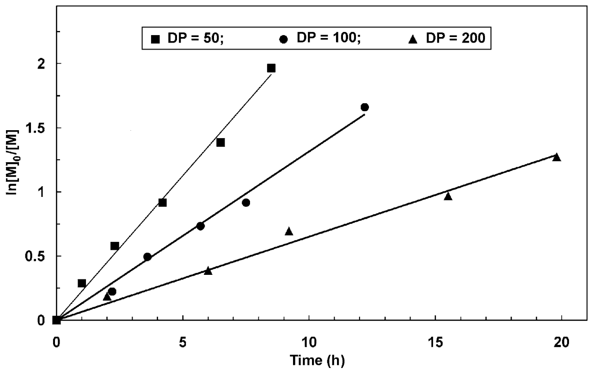


Fig. 3. Plots of $\ln[M]_0/[M]$ versus t for the ATRP of MEA in bulk at 60 °C catalyzed by CuBr/PMDETA for different concentrations of initiator, $[\text{MBP}]_0$. ($[\text{MEA}]_0 = 7.8$ M; $[\text{MEA}]_0/[\text{MBP}]_0 = 50/1, 100/1, 200/1$).

With increasing concentration of initiator, MBP, the apparent rate constant of polymerization (k_{app}), determined from kinetic slopes, also increases. The dependence of the apparent rate of polymerization on the concentration of initiator was elucidated by plotting $\ln k_{\text{app}}$ against $\ln[\text{MBP}]_0$ (Fig. 4). The slope of the line indicated an apparent 0.90 order with respect to the initiator (MBP) in this system.

To examine the initiator efficiency ($f = M_{\text{n,th}}/M_{\text{n,GPC}}$), the trend in molecular weight distribution data with conversion was investigated for polymerizations with three different concentrations of initiator. As shown in Fig. 5, in all the cases, the evolution of molecular weights and PDI with the conversion was linear indicating towards the controlled nature of polymerization. A good correlation between the theoretical and experimental M_{n} values was achieved

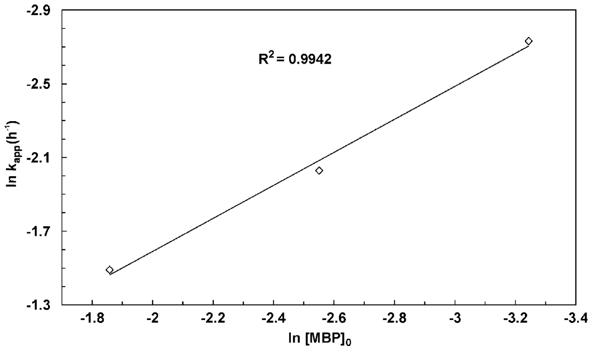


Fig. 4. Dependence of k_{app} on $[\text{MBP}]_0$ ($[\text{MEA}]_0 = 7.8$ M; $[\text{MEA}]_0/[\text{MBP}]_0 = 50/1, 100/1, 200/1$).

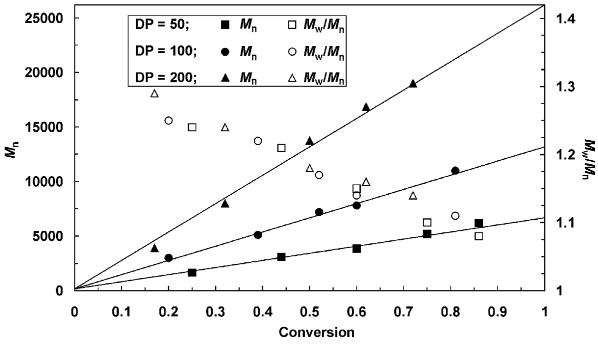


Fig. 5. Dependence of molecular weights and polydisperisites with conversion for the ATRP of MEA in bulk at 60 °C catalyzed by CuBr/PMDETA for different concentrations of initiator, $[\text{MBP}]_0$. ($[\text{MEA}]_0 = 7.8$ M; $[\text{MEA}]_0/[\text{MBP}]_0 = 50/1, 100/1, 200/1$). The solid lines represent the theoretical M_{n} values based on $[\text{MEA}]_0$ and $[\text{MBP}]_0$.

for three different initiator concentrations revealing the good initiator efficiency of MBP for the ATRP of MEA under these conditions.

3.2. Effect of catalyst concentration

Many researchers [45–47] are focusing their attention on studying the performance of ATRP with low catalyst concentrations due to the difficulty in the complete removal of catalyst from the polymer. With the aim of achieving well-defined PMEA by ATRP within a reasonable polymerization time using reduced concentration of catalyst, another experiment was performed in which the catalyst concentration was reduced from 50% to 10% relative to initiator. With 10% catalyst concentration relative to initiator, decrease in the rate of polymerization was observed in comparison with a catalyst concentration of 50% relative to initiator, but it remained well-controlled as revealed by the linear first-order kinetic plot (Fig. 6).

Further support of the living nature of polymerization was obtained from the molecular weight distribution data. The evolution of molecular weight and molecular weight distribution with conversion for different catalyst concentrations was shown in Fig. 7. $M_{n,GPC}$ were found to be in good agreement with $M_{n,th}$ and the PDI remained low throughout the polymerization.

3.3. Effect of solvent

To investigate the effect of solvent on the ATRP of MEA, polymerization of MEA was attempted in ethylene carbonate and toluene (50% v/v) while keeping the other reaction conditions constant at 60 °C. The polymerization in ethylene carbonate was relatively fast as compared to that in toluene as solvent. However, in both the cases, the comparison of M_n and M_w/M_n versus conversion (Fig. 8), showed a linear development of molecular weight with the consumption of monomer and the maintenance of narrow molecular weight distribution throughout the polymerization. Moreover, $M_{n,GPC}$ were close to the theoretical values. These results indicate that the rate of equilibration between the active radicals and dormant species is fast, and that the termination and other side reactions are insignificant for polymerization of MEA in ethylene carbonate as well as toluene as solvent. The living nature of polymerization in both the solvents was

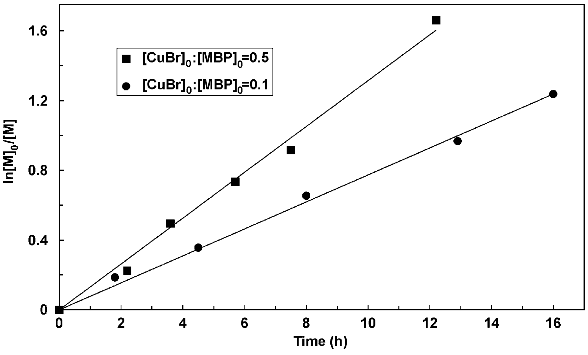


Fig. 6. Plots of $\ln[M]_0/[M]$ versus time for the ATRP of MEA in bulk at 60 °C with CuBr/PMDETA at different $[CuBr]_0/[MBP]_0$ ratio ($[MEA]_0 = 7.8$ M; $[MEA]_0/[MBP]_0 = 100/1$).

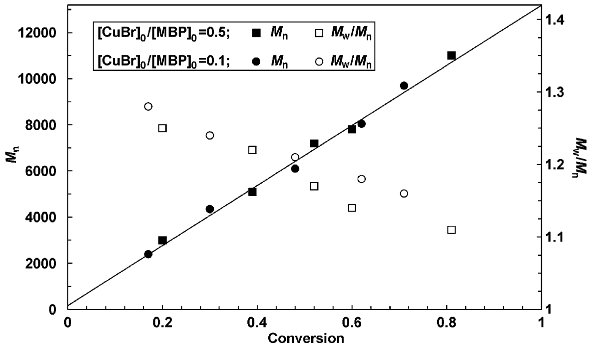


Fig. 7. Evolution of M_n and M_w/M_n versus conversion for the ATRP of MEA in bulk at 60 °C with CuBr/PMDETA at different $[CuBr]_0/[MBP]_0$ ratio ($[MEA]_0 = 7.8$ M; $[MEA]_0/[MBP]_0 = 100/1$). The solid lines represent the theoretical M_n values based on $[MEA]_0$ and $[MBP]_0$.

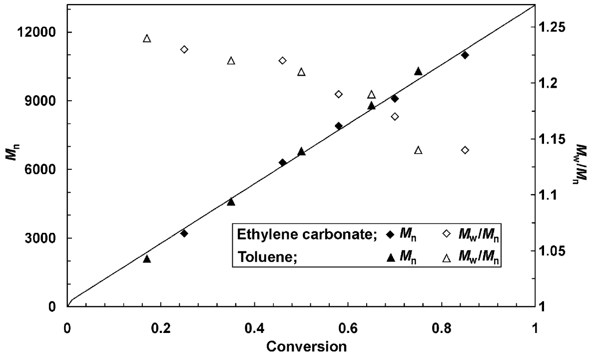


Fig. 8. Dependence of molecular weight, $M_{n,GPC}$ and molecular weight distribution, M_w/M_n on conversion for the ATRP of MEA initiated by MBP and catalyzed by CuBr/PMDETA at 60 °C in ethylene carbonate and toluene (50% v/v) as solvent. ($[MEA]_0 = 5.2$ M; $[MEA]_0:[MBP]_0:[CuBr]_0:[PMDETA]_0 = 100:1:0.5:0.5$). The solid lines represent the theoretical M_n values based on $[MEA]_0$ and $[MBP]_0$.

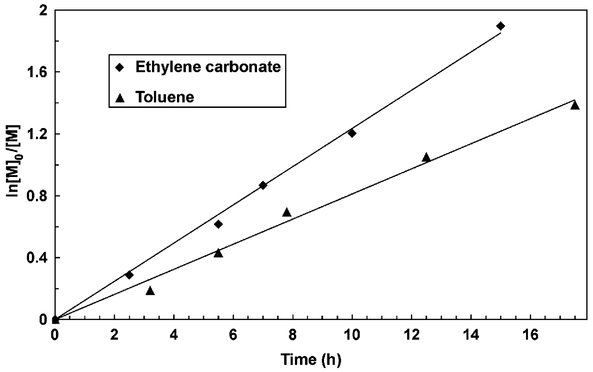


Fig. 9. Semilogarithimic kinetic plot for the ATRP of MEA initiated by MBP and catalyzed by CuBr/PMDETA at 60 °C in ethylene carbonate and toluene (50% v/v) as solvent. ($[MEA]_0 = 5.2$ M; $[MEA]_0:[MBP]_0:[CuBr]_0:[PMDETA]_0 = 100:1:0.5:0.5$).

further confirmed by the linearity observed in the kinetic plot as shown in Fig. 9.

3.4. Analysis of the end groups

End-group analysis of polymers by ATRP is important because the polymer chains with halogen end groups act as a macroinitiator. It can be reactivated in the presence of the ATRP catalyst system to initiate the polymerization of the second monomer to form a block, graft, star polymers, etc., depending on the position and number of initiation sites. Hence, the usage of NMR in analysis of end group to reinstate the living nature of polymerization was explored. The presence of Br at the chain end for PMEA was confirmed by end-group analysis with the aid of $^{13}C\{^1H\}$ NMR spectrum (Fig. 10) of the homopolymer having $M_n = 3100$ and PDI = 1.15. The methine carbon of the CH–Br unit was found to resonate at ~55 ppm, hence confirming the presence of end group.

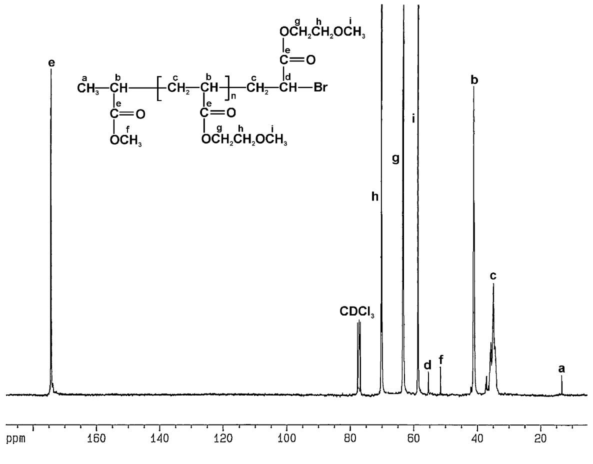


Fig. 10. $^{13}C\{^1H\}$ NMR spectra of PMEA ($M_n = 3100$, Table 1: entry 7) synthesized by ATRP, showing Br as the end group.

3.5. Polymerization mechanism by tacticity

For PMEA, the isotactic parameter (σ) was calculated by the integration of the signals at 40.88 and 41.10 assigned to mm, and (mr + rr) respectively, of the backbone methine resonance signal in the $^{13}C\{^1H\}$ NMR spectrum. The value of σ was found to be 0.23, which is in agreement with the value found for the homopolymers synthesized by free radical polymerization, hence indicating that the reactivity and stereochemistry of a growing radical obtained by controlled and conventional techniques are equivalent.

3.6. Chain extension experiment

Due to the insolubility of pure polyacrylonitrile segments in the solvents, commonly used in ATRP such as xylene, anisole, and toluene or in monomers (acrylonitrile, acrylates), the chain extension experiment using PMEA macroinitiator for the ATRP of acrylonitrile (AN) was conducted with ethylene carbonate as solvent. It is well-documented that to attain high blocking efficiency, the rate of cross-propagation should be comparable to the rate of the subsequent propagation reaction, which can be achieved by using halogen exchange technique. Thus, block copolymerization of PMEA with AN was attempted using halogen exchange technique with CuCl/bpy as catalyst system in ethylene carbonate at 70 °C. Table 1 shows the reaction conditions and results for the block copolymerization with acrylonitrile (AN) using PMEA macroinitiators of different molecular weights.

GPC profile of the block copolymer, as given in Fig. 11, showed that the obtained curves are monomodal and symmetrical in nature with no traces of residual macroinitiator. The clean and clear shift towards higher molar mass region with monomer conversion indicated towards the successful formation of poly(2-methoxy ethyl acrylate)-*block*-poly(acrylonitrile), (PMEA-*b*-PAN). To check the macroinitiator efficiency, concentration of macroinitiator was varied with respect to monomer. Both molecular weight distribution (Fig. 12) as well as

Table 1
Block copolymerization from PMEA to AN at 70 °C by ATRP (bold entries describe macroinitiators PMEA)

No.	Polymer	[monomer]/ [initiator]/[CuX]/[ligand]	Time (h)	Conv (%)	$M_{n,th}(10^4)$	$M_{n,GPC}(10^4)$	$M_{n,NMR}(10^4)$	PDI
1[a]	**PMEA**	**200:1:0.5:0.5**	**19.8**	**72**	**1.89**	**1.90**	–	**1.14**
2[b]	PMEA-*b*-PAN	400:1:0.5:1.5	20	60	3.17	3.15	3.16	1.21
3[a]	**PMEA**	**100:1:0.5:0.5**	**12.2**	**81**	**1.07**	**1.10**	–	**1.11**
4[b]	PMEA-*b*-PAN	200:1:0.5:1.5	2	20	1.31	1.32	1.34	1.19
5[b]	PMEA-*b*-PAN	200:1:0.5:1.5	5	41	1.54	1.52	1.53	1.22
6[b]	PMEA-*b*-PAN	200:1:0.5:1.5	9.5	65	1.79	1.80	1.81	1.20
7[a]	**PMEA**	**50:1:0.5:0.5**	**2.3**	**44**	**0.30**	**0.31**	–	**1.15**
8[b]	PMEA-*b*-PAN	80:1:0.5:1.5	7.5	65	0.59	0.60	0.59	1.29
9[a]	**PMEA**	**50:1:0.5:0.5**	**8.5**	**86**	**0.58**	**0.62**	–	**1.08**
10[b]	PMEA-*b*-PAN	150:1:0.5:1.5	9.9	70	1.18	1.15	1.16	1.27
11[b]	PMEA-*b*-PAN	300:1:0.5:1.5	17	68	1.70	1.63	1.65	1.29
12[b]	PMEA-*b*-PAN	600:1:0.5:1.5	32.5	70	2.85	2.95	2.92	1.25

[a] PMEA series, monomer = MEA, initiator = MBP, CuX = CuBr, and ligand = PMDETA.

[b] PMEA-*b*-PAN series, monomer = AN, initiator = PMEA–Br (each block copolymer uses the PMEA listed immediately above the copolymer in the table as macroinitiator), CuX = CuCl, and ligand = bpy.

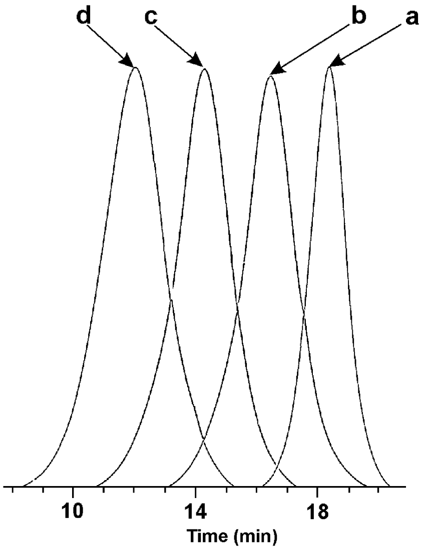


Fig. 11. GPC traces for block copolymerization of AN initiated by PMEA macroinitiator in ethylene carbonate at 70 °C. ($[AN]_0 = 15.2$ M; $[AN]_0$:$[PMEA]_0$:$[CuCl]_0$:$[bpy]_0$ = 200:1:0.5:1.5). Chromatograms a, b, c, and d corresponds to the entries 3, 4, 5, and 6 in Table 1.

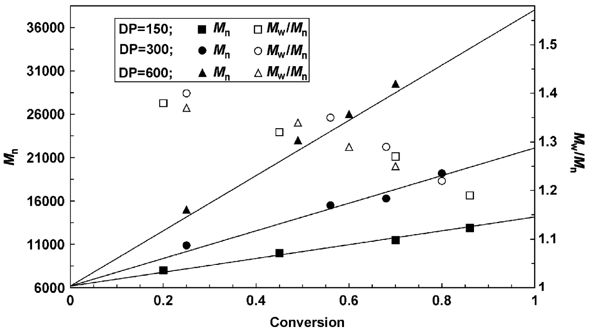


Fig. 12. Evolution of molecular weight and polydispersities as a function of conversion for block copolymerization of AN initiated by PMEA macroinitiator in ethylene carbonate at 70 °C for various DP. ($[AN]_0 = 15.2$ M; $[AN]_0/[PMEA]_0$ = 150/1, 300/1, 600/1; (Table 1: entries 10, 11, and 12)). The solid lines represent the $M_{n,th}$ values based on $[AN]_0$ and $[PMEA]_0$.

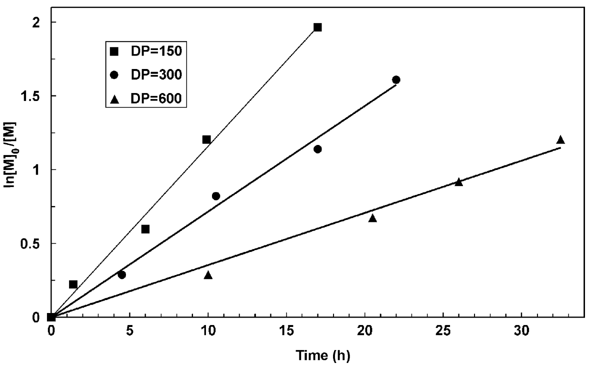


Fig. 13. Plots of $\ln[M]_0/[M]$ versus t for block copolymerization of AN initiated by PMEA macroinitiator in ethylene carbonate at 70 °C for various DP. ($[AN]_0 = 15.2$ M; $[AN]_0/[PMEA]_0$ = 150/1, 300/1, 600/1; (Table 1: entries 10, 11, and 12)).

kinetic studies (Fig. 13) was linear confirming good efficiency of PMEA macroinitiator.

3.7. Determination of composition of PMEA-b-PAN

The composition of PMEA-*b*-PAN was elucidated by ^{1}H NMR spectrum (Fig. 14). The molar compositions were determined by correlating the relative intensities of the resonance signals at 4.4 ppm (attributed to oxymethylene (–OCH$_2$–) protons from

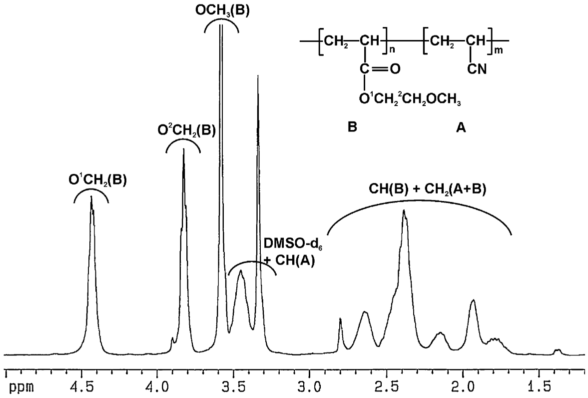


Fig. 14. ^{1}H NMR spectrum of block PMEA-*b*-PAN copolymer ($M_n = 6000$, Table 1: entry 8) synthesized by ATRP.

the MEA unit) and those between 1.7 and 2.7 ppm (due to the backbone methylene and methine protons from MEA unit and backbone methylene protons from AN unit) using the following expression:

$$F_A = \frac{2M - 3N}{2M - N}$$

where, F_A is the molar fraction of acrylonitrile unit in the block copolymer, N is the area under the resonance signal of oxymethylene protons from the MEA unit, M is the area under the resonance signals of the backbone methylene and methine protons from MEA unit and backbone methylene protons from AN unit.

On the basis of molar fraction composition, the molecular weights of the PMEA-*b*-PAN copolymers were calculated using

$$M_{n,NMR} = M_{n,PMEA-Br} + \left[\frac{F_{AN}}{1 - F_{AN}} \times M_{n,PMEA-Br} \times \frac{M_{AN}}{M_{MEA}}\right]$$

where, $M_{n,PMEA-Br}$ is the molecular weight of PMEA macroinitiator as determined using GPC, M_{AN} and M_{MEA} are the molecular weight of AN and MEA, respectively. The $M_{n,NMR}$ for all the diblock copolymers are listed in Table 1 and were found to be in good agreement with $M_{n,th}$ and $M_{n,GPC}$.

4. Conclusions

The optimization of the reaction conditions for the ATRP of MEA has been done successfully. The initiator, MBP, proved to be highly efficient for the ATRP of MEA. With low catalyst concentration of 10% relative to initiator, the polymerizations were well-controlled. The investigation of kinetics as well as molecular weight distribution data indicated the living characteristics of polymerization of MEA in both ethylene carbonate and toluene as solvent. The end-group analysis of PMEA using the $^{13}C\{^1H\}$ NMR spectra, confirmed the presence of bromide chain end functionality. The σ value calculated using $^{13}C\{^1H\}$ NMR spectra for PMEA, indicated that free radical mechanism was being followed. PMEA-*b*-PAN copolymers have also been successfully synthesized by ATRP using PMEA macroinitiators of different molecular weights. The kinetic studies, monomodal nature of GPC curves obtained for these block copolymers confirmed the synthesis of well-defined block copolymers.

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