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NITROXIDE-MEDIATED POLYMERIZATION OF ADAMANTYL-FUNCTIONAL METHACRYLATES FOR 193 NM PHOTORESISTS

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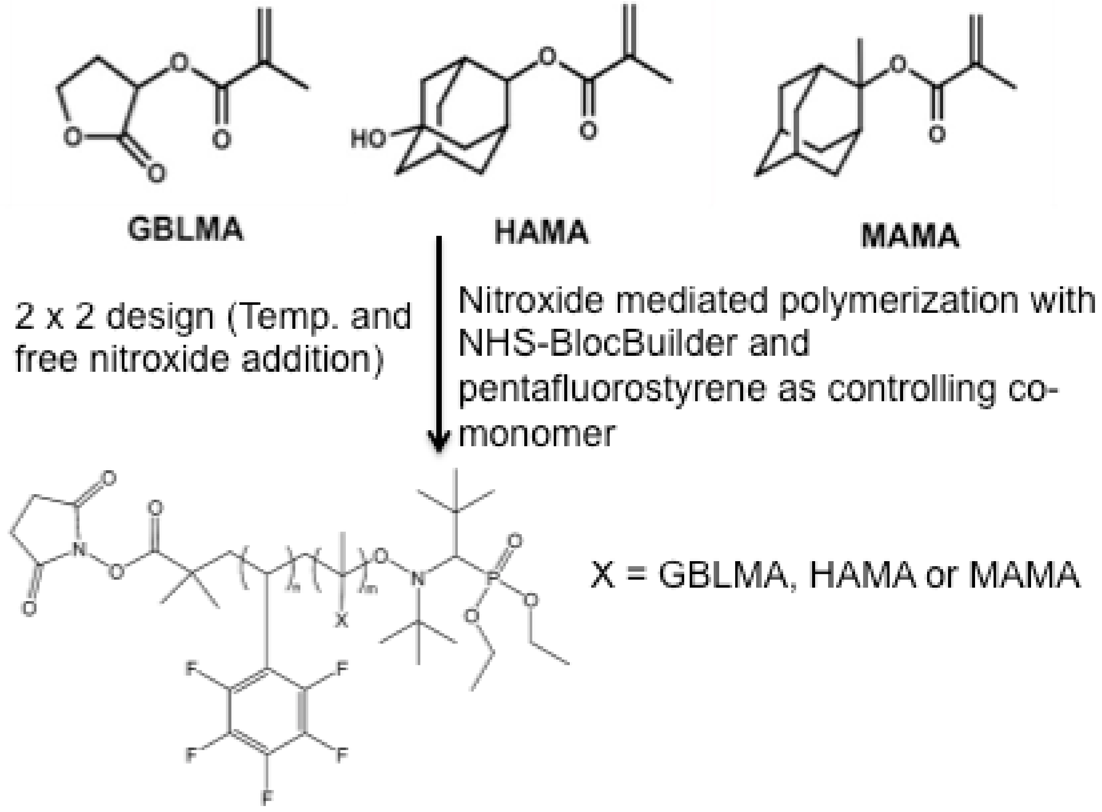
ABSTRACT

Three different methacrylic monomers (γ-butyrolactone methacrylate (GBLMA), 3-hydroxyl-1-adamantyl methacrylate (HAMA) and 2-methyl-2-adamantyl methacrylate (MAMA)), that are most often terpolymerized for 193 nm photoresists, were studied individually by nitroxide mediated polymerization (NMP) with succinimidyl ester terminated BlocBuilder (NHS-BlocBuilder) using a small fraction ~ 5 mol% in the initial mixture of 2,3,4,5,6 pentafluorostyrene (PFS) controlling co-monomer. The copolymerizations were done in 35 wt% dioxane solution and were studied as functions of temperature (75 versus 90 °C) and added free SG1 nitroxide (none versus SG1:NHS-BlocBuilder molar ratio ≈ 0.15) with the objective of minimizing the dispersity ($\overline{M}_w/\overline{M}_n$). MAMA/PFS copolymerizations were not strongly influenced by temperature or addition of free nitroxide, with relatively linear number average molecular weight $\overline{M}_n$ versus conversion plots and $\overline{M}_w/\overline{M}_n$= 1.28-1.55. Further, MAMA/PFS polymerization kinetics was notably slower compared to GBLMA or HAMA copolymerizations with PFS. For GBLMA/PFS and HAMA/PFS copolymerizations, $\overline{M}_w/\overline{M}_n$was reduced the lower temperature of 75 °C but added SG1 did not play a strong role. For GBLMA/PFS, $\overline{M}_w/\overline{M}_n$was reduced from 1.70-1.71 at 90 °C to 1.42-1.50 at 75 °C and for HAMA/PFS, $\overline{M}_w/\overline{M}_n$was reduced from 1.36-1.47 at 90 °C to 1.22-1.31 at 75 °C.

Key phrases: adamantyl methacrylates, nitroxide mediated polymerization, 193 nm photoresist materials.

GRAPHICAL ABSTRACT


GBLMA
HAMA
MAMA
HO
O
2 x 2 design (Temp. and free nitroxide addition)
Nitroxide mediated polymerization with NHS-BlocBuilder and pentafluorostyrene as controlling co-monomer
N
O
P
X
n
m
F
X = GBLMA, HAMA or MAMA

INTRODUCTION

Photolithography is a key process targeted by manufacturers in order to reduce feature sizes of semi-conductor devices. This reduction in size has traditionally been achieved by using shorter wavelengths of light, from 436 nm light down to 193 nm commonly used now. However, the resolutions achieved by 193 nm light is insufficient for current feature sizes, so novel techniques such as immersion lithography and double exposure have been developed to increase the usefulness of 193 nm technology.[1-3] These techniques are also beginning to reach their limit, and therefore new alternatives are being sought that could still use the existing 193 nm photolithography equipment. Conventional photoresists are unable to attain the necessary resolution, and it has become crucial to develop novel types of photoresists that can be used in 193nm ArF photolithography and electron beam lithography.[4-7]

The monomers γ-butyrolactone methacrylate (GBLMA), 3-hydroxyl-1-adamantyl methacrylate (HAMA) and 2-methyl-2-adamantyl methacrylate (MAMA) have desirable properties for use in photoresist polymers. The lactone group of GBLMA plays an important role in etching rate, and facilitates binding to the substrate. The hydroxyl group of HAMA aids in the solubility and stability of the polymer. MAMA is particularly sensitive to 193 nm light, and improves the etching resolution (chemical amplification).[8,9] In photolithography, feature reproduction depends on the photoresist polymer's properties. It has been shown that the reproduction of features depends on factors such as line width roughness (LWR), resolution limit and sensitivity. LWR, depends on the nature of the polymers used, specifically the molecular weight distribution – the narrower the molecular weight distribution, the better is the LWR.[10-13] To accomplish this, conventional free radical polymerization falls short in producing such polymers as molecular weight distributions are typically broad with dispersities > 2 and exhibit poor chain-to-chain compositional control. These characteristics are important as uniform composition and chain length leads to uniform solubility of chains that aid the dissolution process after exposure.

Consequently, methods to produce (co)polymers with the narrow molecular weight distribution and compositional homogeneity are desirable for photoresist materials. A desirable method is controlled radical polymerization (CRP), which uses essentially the same conditions as conventional free radical polymerization. However, it avoids the stringent purification processes involved with ionic polymerizations and is amenable to polymerizations in aqueous media, a feature not possible with "living" polymerization. Further, CRP can combine some monomers or polymer segments that cannot be combined by "living" polymerization. Consequently, variants of CRP such as nitroxide mediated polymerization (NMP), atom transfer radical polymerization (ATRP), reversible addition fragmentation transfer polymerization (RAFT) have been used to make a myriad of polymers/copolymers with controlled microstructures and low dispersities. Not surprisingly, such methodologies have been recently targeted to make photoresist materials for 193 nm photolithography.[14-17]

However, drawbacks exist for both of these methods. RAFT requires the use of thioester-based chain transfer agents (CTAs) to control the polymerization, and the CTA on the chain end in the polymer leave it coloured. This requires removal of the thioester end group to improve transparency required during the photolithography. ATRP requires the use of metallic ligands to control the polymerization, which often leaves the polymer discoloured and requires extensive purification. In response to this problem of removal of metallic or thio-based species, Fleischmann and Percec proposed single electron transfer-living radical polymerization (SET-LRP), as the heterogeneous catalyst used in SET-LRP is much easier to remove compared to ATRP, although some contamination of copper(0) is still possible.[17]

No attempts have however been made to use nitroxide mediated polymerization (NMP) for methacrylic-based photoresist resins with the exception of 5-methacryloxy-2,6, norboranecarbolactone (NLAM).[9] This is likely due to the notion that NMP is only applicable to a certain set of monomers. However, with the development of new nitroxides such as the commercially available BlocBuilder (Arkema), many of the same monomers that are polymerizable by ATRP and RAFT (eg. acrylates and methacrylates) and that are desirable for photoresists, should be polymerized by NMP. BlocBuilder-mediated NMP could control acrylates and methacrylates as well, with a suitable controlling co-monomer for the latter.[18-22] NMP is very attractive compared to RAFT or ATRP as it only requires the nitroxide initiator and heat to effect the polymerization, and the polymers are not coloured by contaminants such as metallic species or sulphur. This lack of discolouration is important, as the polymers need to be transparent for the UV-irradiation to be effective. Usually, the controlling co-monomer is a styrenic and 2,3,4,5,6-pentafluorostyrene (PFS) was chosen as the controlling monomer as it was found to have low absorption in the range near 193 nm and would thus not interfere with the photolithography process.[9] Further, it has potential to be useful in immersion lithography due to the low surface energy of the fluorinated groups.[10] We here propose the use of NMP to make such methacrylic-rich copolymers as 193 nm photoresist candidates using the controlling co-monomer approach by examining the individual copolymerizations of GBLMA, MAMA and HAMA with a low concentration of PFS as controller in the initial mixture. The initiating system is typical for such methacrylate-rich compositions. Such polymerizations previously were performed at relatively low temperature with BlocBuilder and a small excess of free SG1 nitroxide, (typically 10 mol% of free SG1 to BlocBuilder).[18] Noticeably, however, we employed the succinidimidyl ester terminated form of BlocBuilder, NHS-BlocBuilder, which decomposes about 15 times faster than BlocBuilder, and thus mimics the effect of having additional free nitroxide at the beginning of the polymerization.[23] We earlier studied a combination of all three methacrylates with various controllers and found temperature to be an important factor.[24] Our study here was to establish the effect of temperature and additional free SG1 nitroxide to minimize dispersity and to see if control of one monomer was better than others. We still examined the use of additional SG1 relative to NHS-BlocBuilder, as it was useful in reducing the Đ substantially for some acrylate polymerizations with NHS-BlocBuilder.[25]

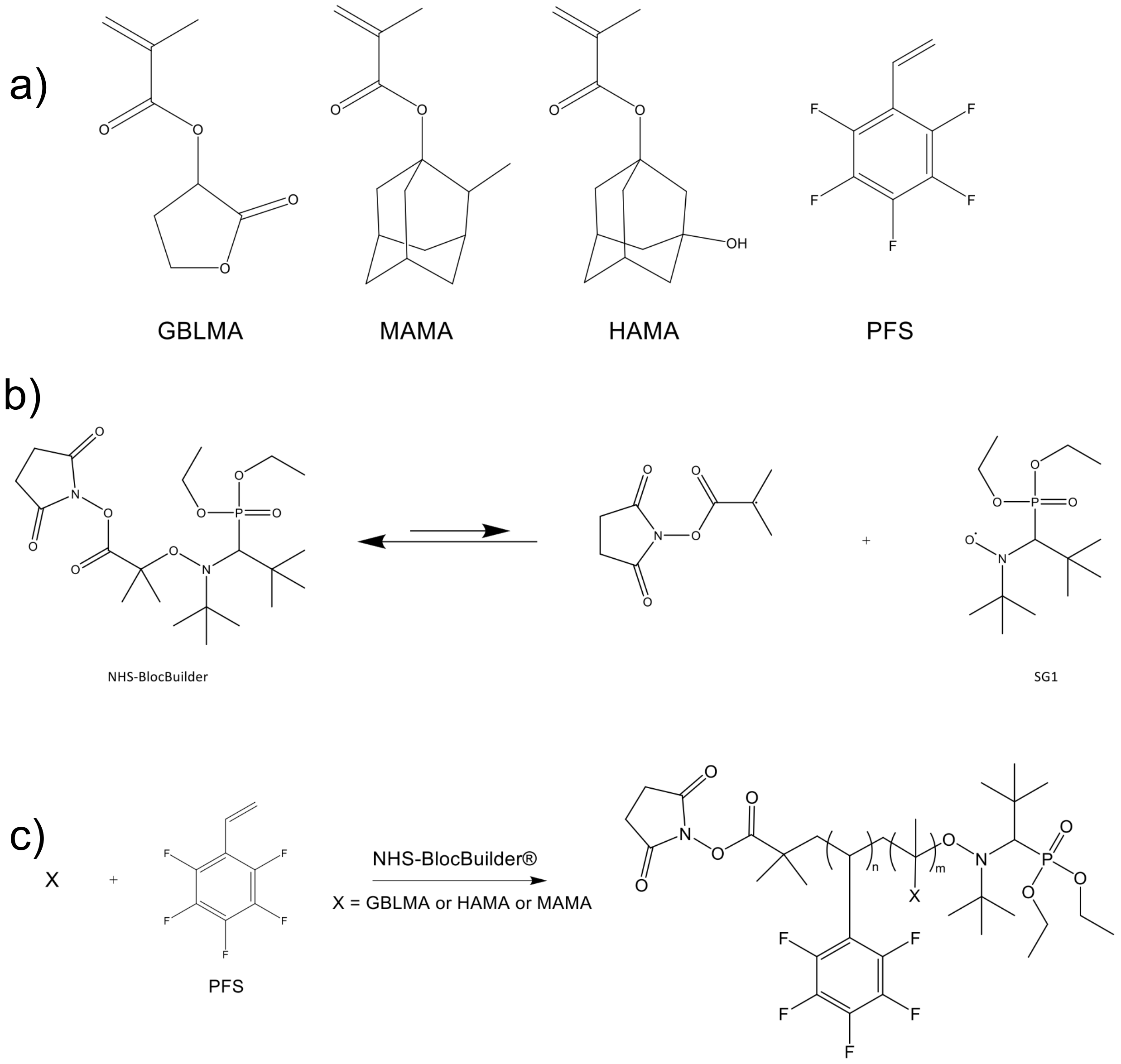


Figure 1. Monomers used for the nitroxide mediated polymerization (a) using NHS-BlocBuilder (b) of methacrylate-rich compositions using the controlling co-monomer approach (c).

EXPERIMENTAL SECTION

Materials

α-γ-butyrolactone methacrylate (GBLMA, 99%) was kindly donated by PCAS Canada, as a white solid. 3-hydroxyl-1-adamantyl methacrylate (HAMA, 99.8%) and 2-methyl-2-adamantyl methacrylate monomers (MAMA, 99.8%) were provided by Osaka Organic Chemical, as white powders. 2,3,4,5,6-pentafluorostyrene (PFS, 99%) was purchased from Oakwood Chemical as a clear liquid. N-(2-Methylpropyl)-N-(1-diethylphosphono-2,2-dimethylpropyl)-O-(2-carboxylprop-2-yl) hydroxylamine (99%, BlocBuilder®) was received from Arkema. N,N'-dicyclohexylcarbodimide (DCC, 99%) was received from Sigma-Aldrich and used in conjunction with BlocBuilder® to synthesize the succinimidyl ester terminated alkoxyamine BlocBuilder (NHS-BlocBuilder) (Scheme 2) using the same procedure as described by Vinas et al.[23] Dioxane (99%) and Tetrahydrofuran (99.8%, HPLC grade) were purchased from Fisher Scientific. N,N-dimethylformamide (99%) was purchased from Acros Organics. All chemicals were used as received; there was no additional purification of monomers done.

Synthesis of Methacrylate-2,3,4,5,6-Pentafluorostyrene Statistical Copolymers

The syntheses of GBLMA, HAMA and MAMA copolymers with PFS were all conducted using the same experimental apparatus. Methacrylate monomer, PFS (~ 10 mol% in the initial composition) NHS-BlocBuilder initiator, and the solvent dioxane, as well as free nitroxide SG1 (10% mol initiator) for the trials which required it, were weighed and transferred to a three-necked round bottom reactor, along with a magnetic stir bar. The reactor was sealed with rubber septa, and fitted with a thermocouple. The reactor was then placed on a heating mantle and secured to a condenser of ethylene glycol water at 4 °C. A nitrogen gas purge needle was also inserted into the reactor. Each set of copolymerizations was done as a 2x2 design with temperature (75 ºC versus 90 ºC) and additional free nitroxide (none versus 10 mol% relative to NHS-BlocBuilder).

For GBLMA - Trial 2 (see Table 1), 4.9123 g (29.0 mmol) of GBLMA monomer, 0.6097 g (3.14 mmol) of PFS (9.8 mol% PFS relative to GBLMA), 0.1075 g (0.22 mmol) of NHS-BlocBuilder, and 16.82 g (0.19 mol) of dioxane were weighed and transferred to a 25 ml reactor with a stir bar and heating mantle. The concentration of monomers in solution was 25 wt% and this was held in all cases. The thermocouple connected to a temperature controller was placed inside a thermal well and connected to one of the necks. A mixture of glycol/water (90/10 vol%) at a temperature of 5 ºC was circulated (NESLAB RTE 740 refrigerating circulator) through the condenser connected to one of the necks of the reactor to prevent any evaporation loss of monomers and/or solvent. The system was purged with nitrogen gas at approximately 3 psi for about 20 minutes, with the needle submerged into the liquid. The flow rate was then decreased to permit mild bubbling, and the needle was raised above the liquid. The temperature was then set to 90 °C and the rate at which the solution heated up to the set point was about 8 °C min^{-1}. Setting time zero to be when the system reached 90 °C, 0.2 ml samples were taken every 30 minutes for gravimetric and GPC analysis. The syringe was rinsed in acetone after each sample of GBLMA/PFS copolymer mixture (THF was used instead for HAMA and MAMA polymerizations). The reaction was stopped after 3.5 hours by reducing the temperature. The final product was precipitated in an appropriate non-solvent (methanol for GBLMA and MAMA-based copolymers, diethyl ether or acetone for HAMA-based copolymer) before being dried under vacuum overnight at 60 °C and collected. Yield = 4.38 g. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) for GBLMA/PFS: (ppm) 5.4 (s, -C*H*-C=O), 4.2 (d, $-CH-CH_2-C\mathit{H_2}-O-C=O$), 2.8 (s, $-CH-C\mathit{H_2}-CH_2-O-C=O$), 1.0-2.0 (m, backbone protons); $\overline{M}_n$ = 24.9 kg mol^{-1}, $\overline{M}_w/\overline{M}_n$ = 1.70 (GPC, THF, 40 °C, relative to linear PMMA standards).

Chain Extension

1.339 g (0.094 mmol) of macroinitiator (1_HAMA-PFS10% product, $\overline{M}_n$ = 14.4 kg mol^{-1}, $\overline{M}_w/\overline{M}_n$ = 1.38, see Table 1), 5.364 g (27.365 mmol) of PFS and 16.2 g (184 mmol) of dioxane were weighed out and transferred to a 50 ml reactor with stir bar and heating mantle. The thermocouple connected to a temperature controller was placed inside a thermal well and connected to one of the necks. A mixture of glycol/water (90/10 vol%) at a temperature of 4 °C was circulated (NESLAB RTE 740 refrigerating circulator) through the condenser connected to one of the necks of the reactor to prevent any evaporation loss of monomers and/or solvent. The system was purged with nitrogen gas at approximately 3 psi for around 20 minutes, with the needle submerged into the liquid. The flow rate was then decreased and the needle was raised above the liquid. The temperature was then set to 100 °C, and the reaction allowed to proceed for until the solution became viscous. Samples were periodically removed for molecular weight determination. The reaction medium only become soluble after a temperature of 85 °C was reached. The solution became progressively cloudier after about 6 h. Polymerization continued for 20 h at 100°C after which heating was ceased. Additional solvent was used to remove the viscous product from the reactor and then the final product was precipitated in diethyl ether and dried in a vacuum oven overnight at 60 °C. The final yield was 2.70 g and the $\overline{M}_n$ = 28.3 kg mol^{-1}, $\overline{M}_w/\overline{M}_n$ = 1.73 (GPC, THF, 40 °C, relative to linear PMMA standards). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) for HAMA/PFS-10-b-PFS: (ppm) 1.7 (adamantyl $-CH_2-$), 0.85 (s, $-CH_3$ backbone).

Characterization

Conversion was determined via gravimetry. After experimenting with precipitating and decanting the gravimetric samples, it was found that decanting often resulted in poorer reproducibility. The most consistent gravimetric results were obtained from a precipitation in non-solvent, followed by evaporation in air. A subsequent dissolution, precipitation, and evaporation was also done. The samples were then dried overnight in a vacuum oven set at 50 °C and weighed the following morning. The ^{1}H NMR measurements were done with a 400 MHz Varian VNMRS spectrometer using $CDCl_3$ solvent. The molecular weight distribution was measured using gel permeation chromatography (GPC, Water Breeze) with HPLC grade THF as the mobile phase. A mobile phase flow rate of 0.3 mL min^{-1} was applied and the GPC was equipped with 3 Waters Styragel® HR columns (HR1 with molecular weight measurement range of 10^2 -5 x 10^3 g mol^{-1}, HR2 with molecular weight measurement range of 5 x 10^2 -2 x 10^4 g mol^{-1} and HR4 with molecular weight measurement range 5 x 10^3-6 x 10^5 g mol^{-1}) and a guard column was used. The columns were heated to 40 °C during the analysis. The molecular weights were determined by calibration relative to linear narrow molecular weight distribution poly(methyl methacrylate) (PMMA) standards from Varian, with the following molecular weights ([=] g mol^{-1}): 1000, 2710, 5000, 10 900, 27 600, 60 150, 138 600, 298 900, 679 000, 1 677 000. The GPC was equipped a differential refractive index (RI 2410) detector.

RESULTS AND DISCUSSION

The results of the 2x2 experimental designs for each of the three copolymerization systems is summarized in Table 1 while the plots of $\overline{M}_n$ and dispersity versus conversion x and the semilogarithmic kinetic plots ($\ln\left[(1-x)^{-1}\right]$ versus time) are listed in Figure 2 for the GBLMA/PFS copolymerizations, Figure 3 for the HAMA/PFS copolymerizations and Figure 4 for the MAMA/PFS copolymerizations. The $\overline{M}_n$ versus conversion plots are useful as they are one supporting method to infer how controlled the polymerization is. A linear dependence of $\overline{M}_n$ versus conversion is expected for truly living polymerizations but it should not be the only criterion as pointed out by Chauvin et al, who described livingness for controlled radical polymerizations more succinctly as testing for chain end fidelity by ESR.[26] Figures 2-4 should be interpreted with some caution. First, the samples were precipitated and recovered, resulting in the washout of some oligomeric species, which would effectively fractionate the sample and thus a higher $\overline{M}_n$ would be reported. Also, the GPC was calibrated relative to poly(methyl methacrylate) standards using a differential refractive index detector and thus the reported $\overline{M}_n$ for the GBLMA, HAMA and MAMA-rich copolymers could vary significantly from that reported in Table 1 and in Figures 2-4. The Mark-Houwink coefficients for poly(GBLMA), poly(HAMA) and poly(MAMA) were not available from literature and thus universal calibration could not be applied. Guillaneuf and Castignolles reported that apparent $\overline{M}_n$ could be misleading in assessing the controlled character of a polymerization. If Mark-Houwink parameters are not available and absolute molecular weight detectors are not available, then solvent quality data like solubility parameters can be used to assess interactions of the samples and calibration standards in a given solvent.[27] There is the possibility of irreversible chain termination occurring in the initial stages of the polymerization, which would effectively lower the number of active chains and thus increase the effective theoretical degree of polymerization. This seems especially plausible for the GBLMA-containing systems shown in Figure 2 as all of the plots, even when the $\overline{M}_n$ versus conversion was linear, were all above the theoretically predicted linear relationship. See *Supporting Information* for GPC traces of all experiments from the 3 copolymerization systems studied.

The $\overline{M}_n$ versus x plots generally revealed poor livingness (non-linearity) for GBLMA and HAMA systems copolymerizations with PFS, with the exception of the lower temperature (75 °C) and with added SG1 (Figure 2b and Figure 3b). MAMA/PFS copolymerizations indicated $\overline{M}_n$

versus x had closer adherence to the theoretical prediction but did start to plateau at early $x \sim 0.2$-0.3 and tailed off to relatively low $\overline{M_n} \approx 5\ 000\ \text{g mol}^{-1}$ in each case. In a parallel manuscript,[24] we described a ternary methacrylate system consisting of GBLMA/HAMA/MAMA compositions (that were selected based on favourable photochemical properties)[15] which reflected generally similar observations except in terms of dispersity of final polymers but better linearity in $\overline{M_n}$ versus x plots with fairly good linear relationships up to $x \sim 0.7$. Perhaps the combination of all three methacrylates helped to balance polymerization kinetics or improve the chain end fidelity (the propensity of the terminal group to be mostly the controlling co-monomer as measured by Charleux and co-workers).[19] This could be conclusively determined by copolymerization studies over a wide range of compositions to determine reactivity ratios and thus find the probability that the chain end is terminated by the controlling co-monomer. There are very few cases studying in detail the reactivity ratios of PFS with methacrylates. Pitois et al. studied the copolymerization of PFS with glycidyl methacrylate (GMA) and measured reactivity ratios $r_{PFS} = 0.38$ and $r_{GMA} = 0.89$,[28] which is fairly typical of styrenics with methacrylates. PFS was also copolymerized with n-phenyl maleimide (PMI) with $r_{PFS} = 0.28$ and $r_{PMI} = 0.86$.[29] Thus, there is no data from PFS copolymerizations to suggest that the chain end would be terminated with a less stable methacrylate group.

Table 1: Summary of Experimental Design for GBLMA, HAMA, and MAMA copolymerizations with PFS Controlling Co-monomer in 35 wt% Dioxane Solution.

Experiment Name	$f_{PFS,0}$	T(°C)	Time (min), X	r	$\overline{M}_n$ (g mol^{-1})	$\overline{M}_w/\overline{M}_n$
1_GBLMA-PFS10%	0.094	75	210, 0.36	0	20500	1.50
2_GBLMA-PFS10%	0.11	75	210, 0.73	0.15	17500	1.42
3_GBLMA-PFS10%	0.098	90	210, 0.76	0	24000	1.71
4_GBLMA-PFS10%	0.097	90	210, 0.46	0.16	24900	1.70
1_HAMA-PFS10%	0.10	75	240, 0.82	0	14400	1.22
2_HAMA-PFS10%	0.10	75	210, 0.70	0.16	11400	1.31
3_HAMA-PFS10%	0.096	90	210, 0.72	0	21000	1.47
4_HAMA-PFS10%	0.094	90	210, 0.46	0.15	21300	1.36
1_MAMA-PFS10%	0.12	75	210, 0.49	0	5200	1.40
2_MAMA-PFS10%	0.13	75	210, 0.42	0.17	4600	1.50
3_MAMA-PFS10%	0.13	90	210, 0.56	0	7800	1.28
4_MAMA-PFS10%	0.13	90	210, 0.57	0.16	6500	1.55

*All target weights at complete conversion were set at 20 000 g mol^{-1}.

X = total conversion as measured by gravimetry

r = initial molar ratio of SG1 to NHS-BlocBuilder

All molecular weights reported relative to linear PMMA standards in THF at 40 ºC.

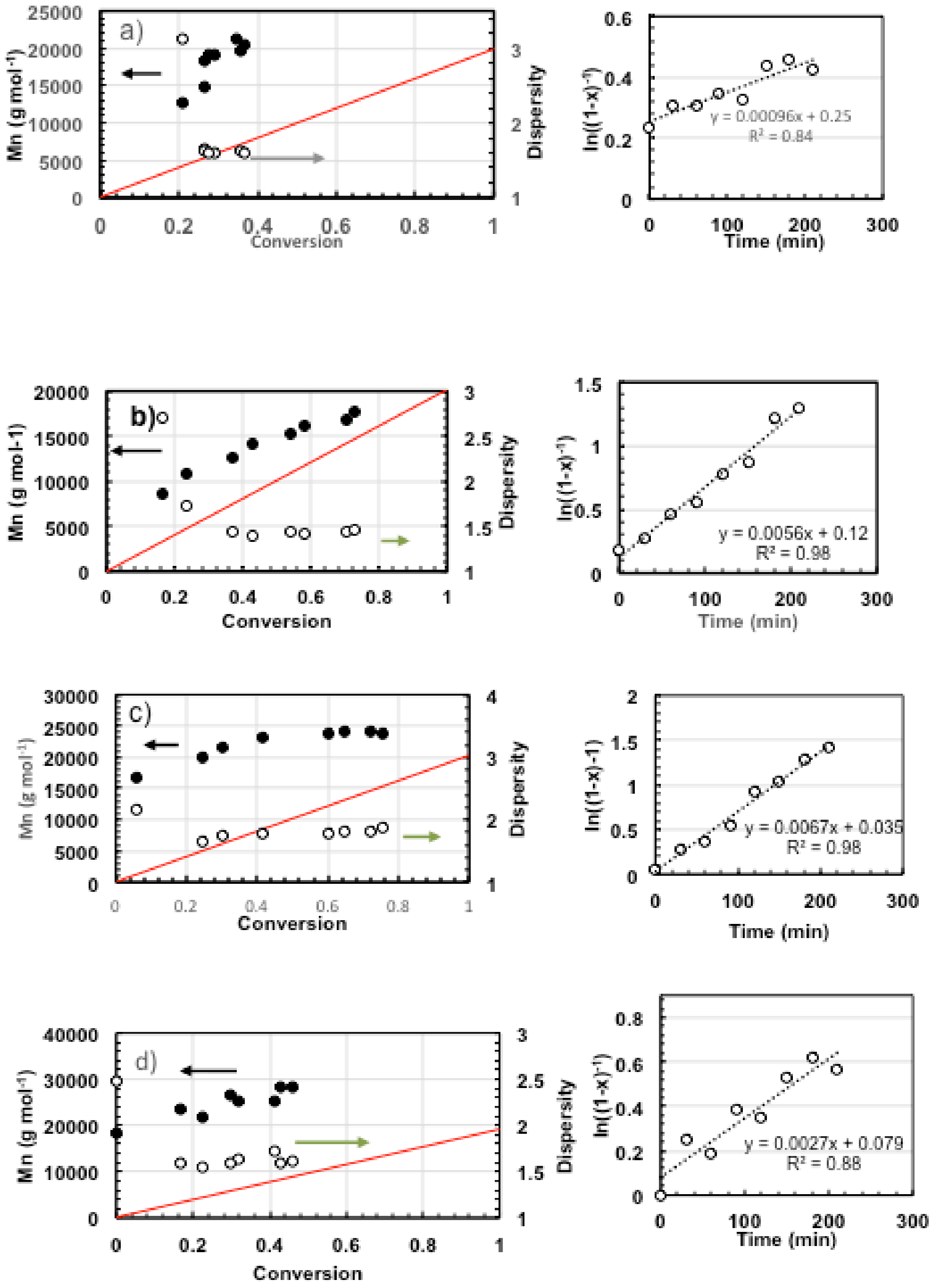


Figure 2. Number average molecular weight $\overline{M_n}$ versus conversion (x) and semi-log plots of $\ln((1-x)^{-1})$ versus time: a) 1_GBLMA-PFS10% – 75 °C, no SG1; b) 2_GBLMA-PFS10% – 75 °C, with SG1; c) 3_GBLMA-PFS10% – 90 °C, no SG1 d) 4_GBLMA-PFS10% – 90 °C, with SG1. The solid line in the $\overline{M_n}$ versus x plots is the theoretical prediction.

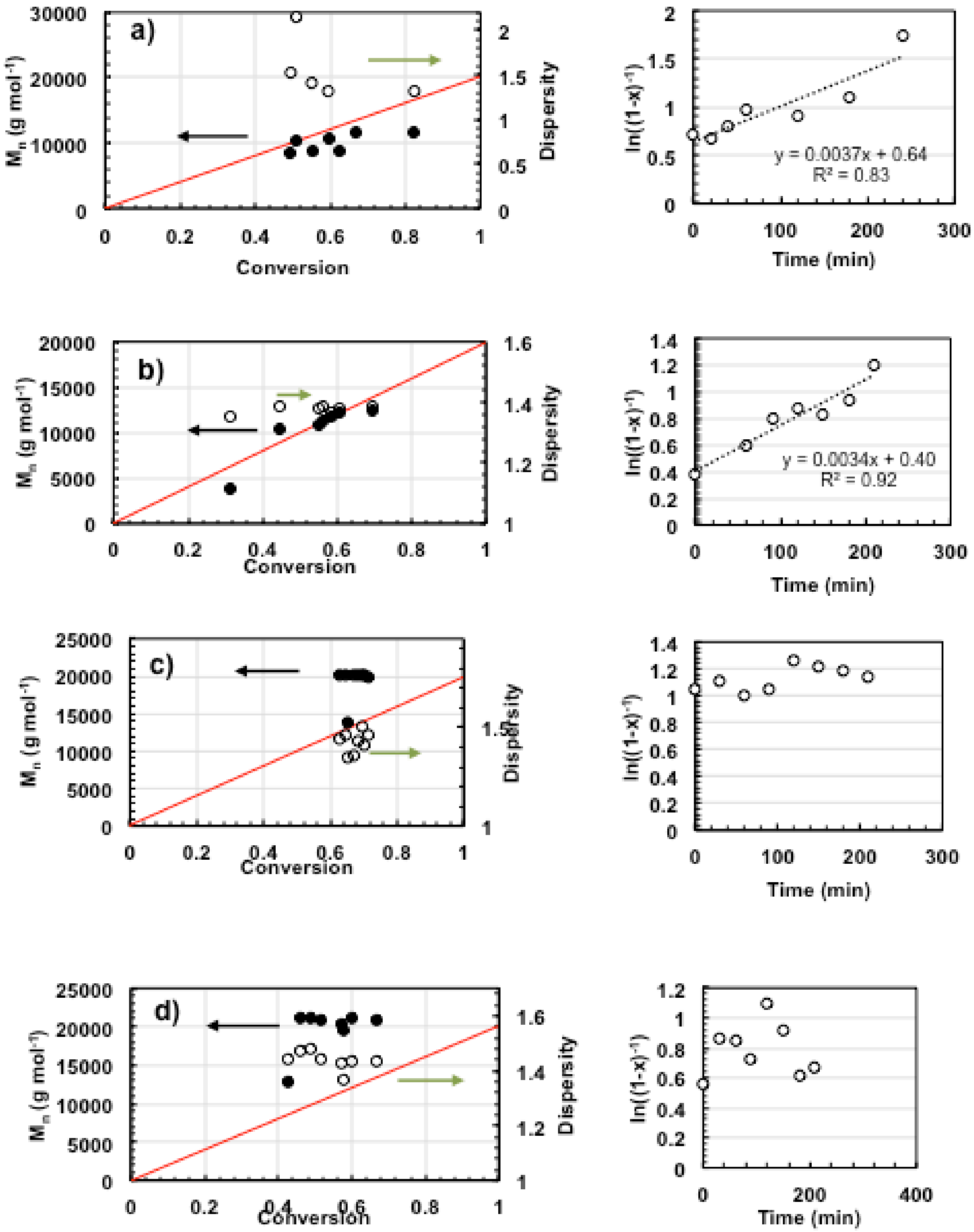


Figure 3. Number average molecular weight $\overline{M}_n$ versus conversion (x) and semi-log plots of ln($(1-x)^{-1}$) versus time: a) 1_HAMA-PFS10 – 75 °C, no SG1; b) 2_HAMA-PFS10 – 75 °C, 10% SG1; c) 3_HAMA-PFS10 – 90 °C, no SG1; d) 4_HAMA-PFS10 – 90 °C, 10% SG1. The solid line in the $\overline{M}_n$ versus x plots is the theoretical prediction.

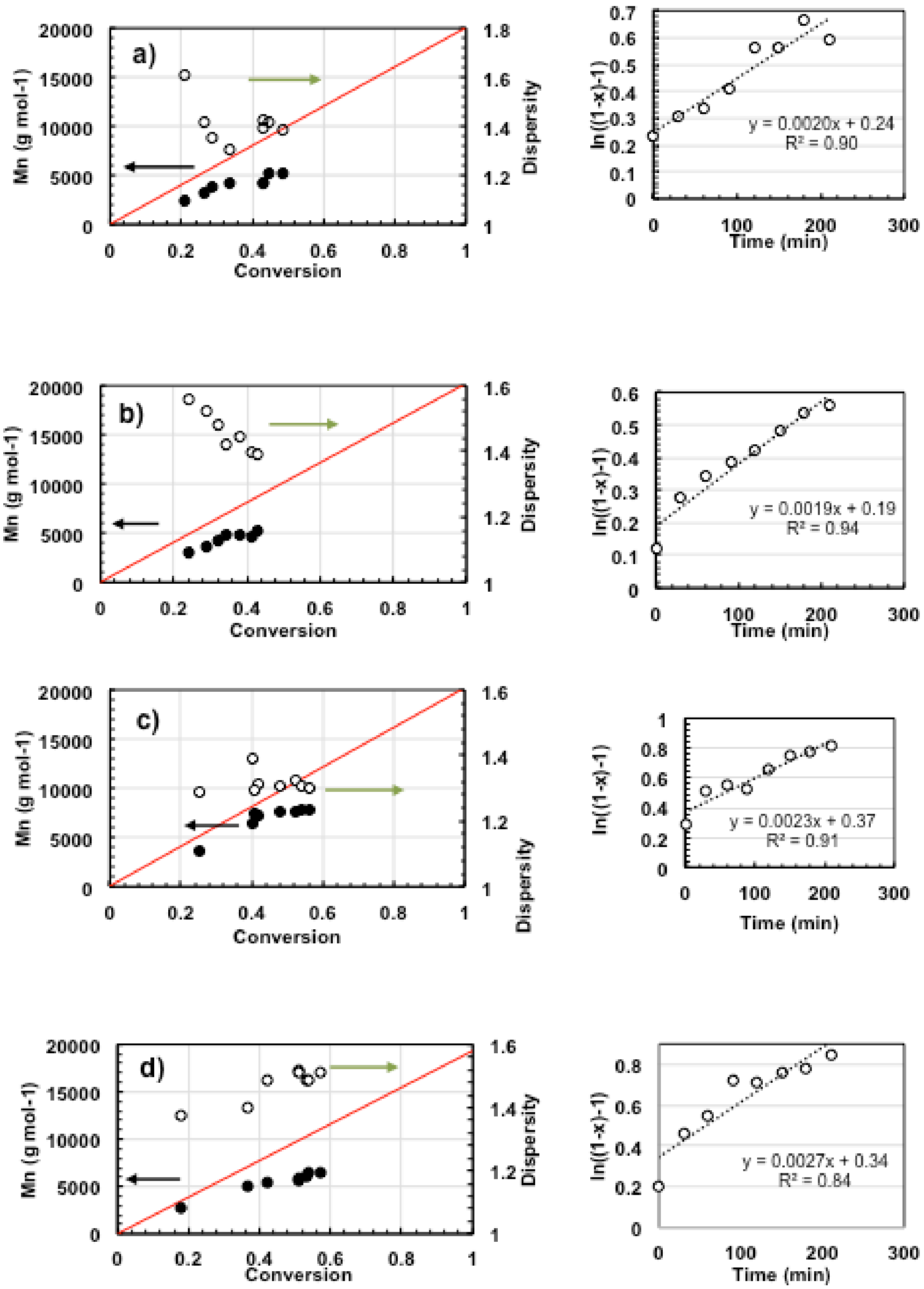


Figure 4. Number average molecular weight $\overline{M}_n$ versus conversion (x) and semi-log plots of $\ln((1-x)^{-1})$ versus time: a) 1_MAMA-PFS10% - 75 °C, no SG1; b) 2_MAMA-PFS10% – 75 °C, 10% SG1; c) 3_MAMA-PFS10% – 90 °C, no SG1; d) 4_MAMA-PFS10% – 90 °C, 10% SG1. The solid line in the $\overline{M}_n$ versus x plots is the theoretical prediction.

Temperature Dependence on Polymerization and Molecular Weight Characteristics

One of the most obvious variables in a polymerization is to control is the temperature. For example, in styrene polymerizations using TEMPO[30] or BlocBuilder-based initiator systems,[31] $\overline{M}_w/\overline{M}_n$ increased with conversion with increasing temperature but was not a significant factor for SG1-based initiators used 4-vinylpyridine polymerization.[32] Here, at lower temperatures, $\overline{M}_w/\overline{M}_n$ was generally lower at identical polymerization times for GBLMA/PFS copolymerizations, even though conversion varied (1.71 to 1.50 without SG1, 1.70 to 1.42 with 10 mol% SG1 in the feed). Even for NHS-BlocBuilder, which decomposes much more rapidly compared to BlocBuilder added SG1 could be used to impart additional control, which we successfully showed for phenyl acrylate homopolymerizations.[25] For example, in all cases for GBLMA/PFS copolymerizations (Figure 2), the plots of $\bar{M}_n$ versus conversion exhibited curvature and plateauing, indicative of irreversible termination. This is particularly reflected in the higher than expected $\bar{M}_n$ at early conversions, with the exception of polymerization done at the lower temperature of 75 ºC with added SG1 to aid control.

For HAMA/PFS copolymerization, temperature dependence dramatically improved the characteristics of the polymerization. By decreasing the temperature from 90 °C to 75 °C, the $\bar{M}_n$ versus conversion plot followed the theoretical line more closely (Figure 3). At 75 °C (Figure 3a and 3b), the $\bar{M}_n$versus conversion plots clearly follow a more linear trend. In both HAMA trials at 90 ºC (Figure 3c and 5d) the $\bar{M}_n$versus conversion plots plateau almost immediately. For 4_HAMA-PFS10% (Figure 3d), 50% conversion is already attained when the reaction mixture reaches the set-point of 90 °C, indicating a rapid, highly uncontrolled chain growth. Thus, for HAMA/PFS copolymerizations, lower temperature was more effective in producing linear $\bar{M}_n$ versus conversion with low dispersity.

For the MAMA polymerizations, increasing the temperature from 75 °C to 90 °C resulted in slightly higher final conversions at the same polymerization time (Figure 4) and thus degrees of polymerization (Table 1). There was no clear difference at the two different temperatures with respect to the $\bar{M}_n$ versus conversion plots, with all showing plateaus becoming apparent at conversions ~ 0.5. The only difference that seemed apparent was the decrease in $\overline{M}_w/\overline{M}_n$ with conversion at the lower temperature.

Effect of Added SG1 Free Nitroxide

Many previous cases for improvement of control in BlocBuilder-mediated NMP have been accomplished by the addition of the free nitroxide in addition to the unimolecular initiator.[33,34] No appreciable SG1 dependence was observed however in the polymerizations of GBLMA, HAMA and MAMA under the conditions studied here at the two levels studied (none versus $r \sim 0.15$). In some cases, excessive SG1 may be detrimental as described by earlier for MMA homopolymerization where the excess SG1 content resulted in disproportionation between the propagating radical chain and the nitroxide[34] (it should be noted that concentrations were far in excess of the $r = [\text{SG1}]_0/[\text{BlocBuilder}]_0 = 0.1$ customarily used for methacrylate polymerizations with a controlling co-monomer). One possible reason that additional free nitroxide did not help in our polymerizations was that the NHS-BlocBuilder mimicked the effect of additional free nitroxide due to its rapid decomposition compared to BlocBuilder (about 15 times faster).[24] Such a rapid relative decomposition would release sufficient free nitroxide to easily trigger the persistent radical effect.

Comparison of Polymerizations as Function of Monomer

As noted in the *Introduction*, GBLMA has been polymerized by ATRP (and its offshoot SET-LRP) and RAFT while HAMA and MAMA have been polymerized by ATRP and RAFT additionally. At 75 °C, HAMA-rich copolymerizations displayed significantly lower $\overline{M}_w/\overline{M}_n$ = 1.22-1.31 despite going to high conversions, compared to the other two monomers. At 90 °C, there was not much differentiation except that GBLMA-rich polymerizations had higher $\overline{M}_w/\overline{M}_n$ = 1.70-1.71 compared to the other two monomers. MAMA-rich copolymerizations were somewhat intermediate in $\overline{M}_w/\overline{M}_n$ compared to the other two monomers (at 75 °C,

$\overline{M}_w/\overline{M}_n$= 1.40-1.50 and at 90 °C $\overline{M}_w/\overline{M}_n$=1.28-1.55 with higher $\overline{M}_w/\overline{M}_n$ with more added free nitroxide, which could suppress the delay the onset of the persistent radical effect.

The MAMA polymerization rates were slower with $\langle k_p \rangle [P\cdot] \approx$ 0.0020 min^{-1} compared to the other two monomers, which had $\langle k_p \rangle [P\cdot] \approx$ 0.0035-0.0067 min^{-1}. In polymerizations of MAMA and GBLMA with SET-LRP, Fleischmann and Percec reported comparatively slower rates for MAMA with $k_p[P\cdot]$ = 0.0015 min^{-1} at 50 °C in ethyl acetate/methanol solutions.[17] It was noted that solvent effects played a role in SET-LRP since polar solvents are preferred to permit efficient disproportionation of the Cu(I) formed and thus some methanol was used to increase the rate of polymerization in the ethyl acetate that is a good solvent for MAMA. Comparison of MAMA or GBLMA apparent rate constants to other monomers was also done. When compared to MMA under identical conditions (dimethylsulfoxide (DMSO) at 50 °C), GBLMA exhibited $k_p[P\cdot]$ = 0.031 min^{-1}, which was slightly higher than MMA ($k_p[P\cdot]$ = 0.018 min^{-1}) and was attributed to the electronic effects from the lactone ring.[17] Thus, the nature of the methacrylate is important. They are all quite structurally different from one another and yet there is no detailed analysis concerning the propagation rate constant for each of these methacrylates available in the literature. This should be an interesting aspect to study in the future vis-à-vis NMP polymerizations of such monomers.

Obviously, direct comparisons with other CRP methods are difficult to apply when comparing kinetics due to initiators, solvents, etc. We can, however, compare the methacrylate-rich copolymerizations by NMP with each other. With the same controller we used (PFS) for the GBLMA, HAMA and MAMA polymerizations, dimethylaminoethyl methacrylate (DMAEMA) and oligo(ethylene glycol) methacrylate OEGMA were polymerized at 110 °C for 6 h.[35] For OEGMA/PFS copolymerizations with $f_{PFS,0}$ = 0.10, conversions were approximately 0.82-0.91, which can be used to estimate $k_p[P\cdot]$ (110 °C) = $\ln\left(\frac{1}{1-x}\right)/t \approx$ 6.4 x 10^{-3} min^{-1}. For DMAEMA/PFS copolymerizations with $f_{PFS,0}$ = 0.10, similar calculations reveal $k_p[P\cdot]$ (110 °C)

$\approx 2.9\ 10^{-4}\ \mathrm{min}^{-1}$, which suggest slower polymerization rates for these monomers compared to the adamantyl methacrylates studied here.

Chain Extensions

Chain extensions with a fresh batch of monomer are very commonly used to assess the chain end fidelity in CRP systems.[36-41] This would subsequently permit the feasibility to produce linear macromolecular architectures like block copolymers but also more complex architectures such as stars[42-44] and dendrimers.[45] For 193 nm photoresists, the key property for reducing line edge roughness is the molecular weight distribution and thus attainment of the lowest $\overline{M}_w / \overline{M}_n$ is key and was thus the focus in this manuscript. We however attempted to check the chain end fidelity by addition of a second batch of monomer to a macroinitiator. A shift in $\bar{M}_n$ was seen from 14 400 g mol^{-1} to 28 300 g mol^{-1} (by GPC relative to PMMA standards) after 20 h polymerization in 70% dioxane solution and the distribution remained monomodal, indicating addition of the second monomer (27% conversion of the second batch of PFS monomer added). $\overline{M}_w / \overline{M}_n$ increased slightly from 1.38 to 1.73 after chain extension, which also indicates some termination in the second block addition, which is usually the case for chain extensions with CRP. The tail obviously indicated some non-active macroinitiator. The ability to retain chain fidelity is useful for block copolymer synthesis with adamantyl-type segments. For example, poly(imide)-b-poly(MAMA) triblocks were shown to be effective for gas permeability applications (the poly(MAMA) contributes low dielectric constant and high free volume to the material)[46] while poly(MAMA)-b-perfluoroalkyl methacrylate diblock copolymers showed promise as resist modifiers due to the preferential wetting of the poly(perfluoroalkyl methacrylate) block for immersion lithography.[47] Thus, we have some indication that the adamantyl-type monomers we used to synthesize photoresist polymers could be applied as block copolymer segments in other applications.

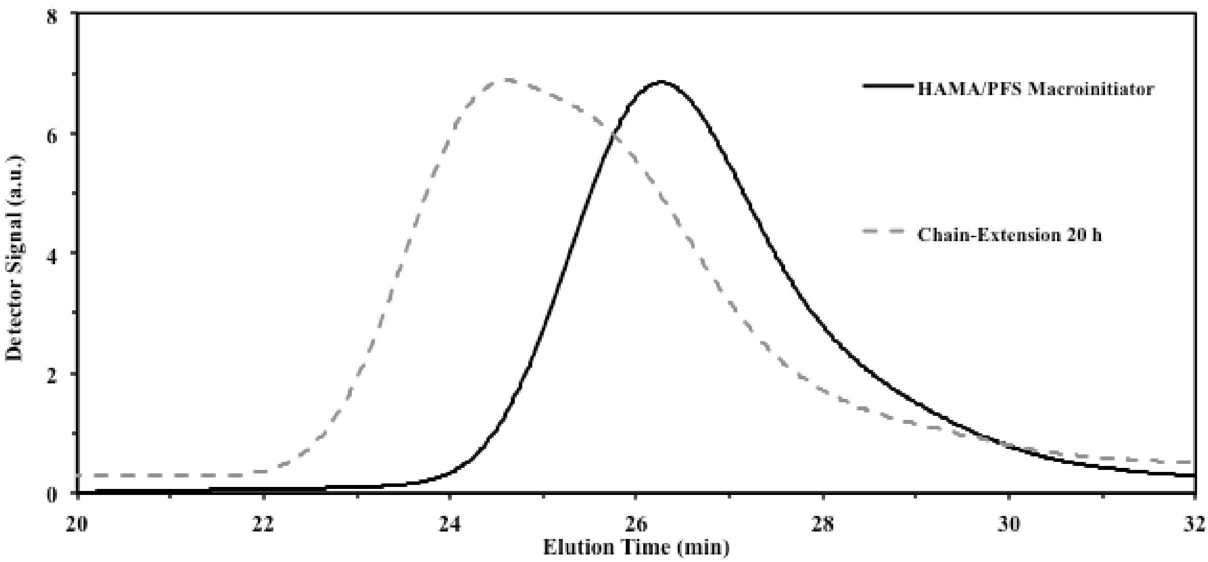


Figure 5. Gel permeation chromatograms of poly(HAMA/PFS) macroinitiator (dashed line $\bar{M}_n$= 14 400 g mol^{-1}, $\overline{M_w}/\overline{M_n}$= 1.38) and chain-extended product with PFS : poly(HAMA/PFS)-*b*-poly(PFS) (solid line, $\bar{M}_n$= 28 300 g mol^{-1}, $\overline{M_w}/\overline{M_n}$= 1.73).

CONCLUSION

Lowering the temperature was most effective on the control of the GBLMA and HAMA polymerizations while added free SG1 nitroxide has little appreciable effect. Compared to HAMA and GBLMA, significant differences in control and dispersity were not observed in MAMA polymerizations when varying the temperature and adding free SG1, and seemed well controlled in the parameter space studied. Dispersities in all cases were reduced compared to conventional radical polymerization, being as low as 1.22 and most < 1.50 with the exception of the GBLMA/PFS copolymerizations which had dispersities ~ 1.70-1.71. The molecular weights achieved were sufficiently lo to be useful for photolithographical testing, with M_n ~ 10 000-20 000 g mol^{-1}. Only GBLMA copolymerizations could not be controlled as well as HAMA or MAMA copolymerizations. This is not expected to profoundly influence the HAMA/MAMA/GBLMA terpolymerizations, which are expected to give ideal photolithographic performance and are the focus of our parallel study.

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