Development of Polymers for Non-CAR Resists for EUV Lithography

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ABSTRACT

Three strategies for approaching the design and synthesis of non-chemically amplified resists (non-CARs) are presented. These are linear polycarbonates, star polyester-*blk*-poly(methyl methacrylate) and comb polymers with polysulfone backbones. The linear polycarbonates were designed to cleave when irradiated with 92 eV photons and high T_g alicyclic groups were incorporated into the backbone to increase T_g and etch resistance. The star block copolymers were designed to have a core that is sensitive to 92 eV photons and arms that have the potential to provide properties such as high T_g and etch resistance. Similarly the polysulfone comb polymers were designed to have an easily degradable polymer backbone and comb-arms that impart favorable physical properties. Initial patterning results are presented for a number of the systems.

Keywords: Non-CAR, non-chemically amplified resists, EUV, polymer architecture, polysulfones, polycarbonates, star block copolymers

1. INTRODUCTION

The development of resist materials that show high sensitivity to EUV radiation and low line-edge roughness (LER) values is becoming of increasing importance for the success of this technology. Due to the possibility that the diffusive path lengths of acids produced by exposure of traditional photoacid generators to EUV photons may play a significant role in the overall LER values of the resists, attention has recently be given to the development of non-chemically-amplified resists (non-CAR). One such approach being investigated by us is the development of polymeric materials that are strongly degraded by EUV without the need for chemical amplification.[1] Here we describe the synthesis of novel linear and branched candidate polymers for high-sensitivity EUV resists.

2. EXPERIMENTAL

2.1 Example Synthesis of Linear Polycarbonates

2.1.1 Synthesis of Bis(imidazole) Carboxylates: 1,3-Adamantanediol (2.00 g, 11.9 mmol) was dissolved in anhydrous THF (50mL) under an atmosphere of argon. Finely divided potassium (1 g) was cut into small pieces and added to the solution, which was refluxed for 2 hr. The mixture was then allowed to cool to 30 ºC and the solution was then transferred to a suspension of 1,1'-carbonyldiimidazole (4.62 g, 28.5 mmol) in anhydrous THF (50 mL) under argon. The mixture was refluxed for 2 hr. The work up was achieved by evaporating THF and adding DCM (200 mL), the solution was washed 3 times with distilled water. The washed organic layer was dried over anhydrous magnesium sulfate and then evaporated to yield the pure product. (3.6 g, 81%. ^{1}H NMR 300 MHz (CDCl$_3$): δ (ppm)) 8.05 (t, 2H), 7.34 (t, 2H), 7.03 (m, 2H), 2.73 (s, 2H), 2.52 (s, 2H), 2.93-2.20 (m, 4H), 1.66, (s, 2H)

2.1.2 Synthesis of Linear Polymer Carbonate: The above *bis*(imidazole) carboxylate (1.00 g, 2.8 mmol) and cyclohexane-1,4-diol (0.347 g, 2.8 mmol) were dissolved in dichloromethane (2.5 mL). 18-crown-6 ether (0.11 g) and anhydrous K$_2$CO$_3$ (2.0 g) were added to the solution under an atmosphere of argon. The suspension was then refluxed for 24 hr. The work up was performed by diluting the mixture with dichloromethane (100 mL) and then centrifuging the suspension. The decanted clear solution was then filtered and most of the solvent was removed by rotary evaporation at reduced pressure. The remaining solution was added drop-wise into a stirred vessel containing methanol (100 mL). A white precipitate was obtained and dried under vacuum at room temperature. ^{1}H NMR 300 MHz (CDCl$_3$): δ (ppm)) 4.59 (m, 2H), 2.48 (s, 1H), 2.36 (s, 2H), 2.05 (m, 8H), 1.87-1.54 (m, 11H), 1.23 (s, 1H); GPC (pSty calibration): Mw 4202, PDI 1.44., DSC T_g 172ºC

2.2 Synthesis of Star Block Copolymers

2.2.1 Synthesis of 6-arm Poly(l-lactide) with BIBB End Groups (One Pot) To a freshly silanized and flame-dried Schlenk vessel, sorbitol (8 mg, 0.04 mmol) and DABCO (23 mg, 0.21 mmol) were added, placed under vacuum and dried at 110 °C for 30 min. The mixture is then cooled to room temperature and l-Lactide (1 g, 6.9 mmol) is added. The Schlenk is then sealed and stirred at 110 °C for 6 hr. After this time the reaction had ceased stirring and formed a colorless solid. The solid was dissolved in dichloromethane (3 mL). Triethylamine (90 μL) was added and the mixture was cooled to 0 °C. BIBB (130 μL) is added drop-wise and then the reaction mixture is allowed to warm to room temperature and stir for 4 hrs. The mixture was then diluted with dichloromethane, washed with water and the organic layer was dried with sodium sulfate and concentrated under reduced pressure. This yielded a white powder that was purified by reprecipitation (890 mg, 89 %, Mn: 43648, PDI: 1.23).

2.2.2 Synthesis of 6-arm Poly(l-lactide)-co-poly(methyl methacrylate) via ATRP Poly(l-lactide)-BIBB (500 mg) and methyl methacrylate (1 ml) were dissolved in toluene (1 ml) and the solution was degassed for ca. 60 min. To this N-(n-hexyl)-2-pyridylmethamine (24 mg in 1 mL of toluene) and copper (I) bromide (12 mg) were added, the vessel sealed and the reaction heated at 90 °C for 4 hr. The reaction was then quenched by opening the vessel to air and the mixture diluted with chloroform. The solution was run through a plug column of alumina to remove the catalyst and was precipitated into a ten-fold excess of methanol. This yielded a fine white powder of poly(l-lactide)-*blk*-poly(methyl methacrylate) (865 mg, 58 %, Mn: 97741, PDI: 1.33).

2.3 Synthesis of Comb block copolymers

2.3.1 ***Typical Synthesis of Poly(methyl methacrylate) via ATRP:*** The MMA monomer (2.5 mL), initiator, ligand and toluene (2.5mL) were placed in a Schlenk flask and degassed using argon for ~10min. The Cu(I)Br was added under positive pressure and the solution degassed for a further 5min at room temperature before being placed in an oil bath at 90°C. After the required time, the reaction was removed from the heat and placed in an ice bath to cool before exposing to air. The ratio of monomer : initiator : ligand : Cu(I)Br was x : 1 : 2 : 1 where 'x' is (desired MW of the polymer)/(MW MMA).

2.4 Exposures

Polymers were dissolved in propylene glycol methyl ether acetate, **no photo-acid generator was added,** and the solutions were spin coated onto silicon wafers with an approximately 2 nm native oxide layer. Wafers were irradiated at PSI and at the soft-X-ray beam-line at the Australian Synchrotron using 92 eV photons.

3. RESULTS & DISCUSSION

In this project we have adopted a rational-design approach to preparation of non-chemically-amplified EUV resists. Firstly we have sought to demonstrate that the relative rates of chain scission of main-chain polymers are the same on exposure to EUV and high energy 1 MeV gamma photons, the latter being readily available to us. This allows us to rapidly screen commercial polymers or materials prepared in our laboratories. Secondly we have proposed that structural units sensitive to cleavage by secondary electrons produced by interaction with 92 eV photons can be identified by the relative sensitivity of small molecules within the ionization chamber of a mass spectrometer. Based on these experiments a quantitative structure-property relations (QSPR) model was proposed and used to guide the selection of structures for synthesis. As described below these materials show promise as non-chemically-amplified resists.

3.1 Design Rules

The primary process occurring in extreme UV lithography is the interaction of the ~100 eV photons with the polymeric resist to generate cationic species and electrons, which in turn produce a population of thermalized secondary electrons. These secondary electrons are captured and the radical anion so-produced degrades to free radical or ionic species. Currently EUV resists exploit analogues of traditional photoacid generators, which are efficient at capturing secondary electrons and which lead to formation of acidic species; these acids then catalyze the deprotection of ester or carbonate groups resulting in a change in solubility of the polymer. In non-CAR by contrast, the primary and secondary processes involve the polymeric component of the resist, and the sensitivity of the resist is directly related to the propensity of the polymer to undergo a change in molar mass as a result of the secondary reactions. For positive-tone resists the sensitivity is directly related to the rate of chain scission on interaction with the EUV photon.

There exists extensive knowledge of the relationship between polymeric structure and the sensitivity of that material to high energy photons, in particular for 1 MeV gamma photons. It is known that the mechanism of degradation of polymers is similar to that described above for EUV and hence it was proposed that gamma radiolysis could be used as a convenient method of screening materials for high sensitivity to EUV. This is particularly important because of the difficulty in obtaining access to EUV photons experienced by many working in this field.
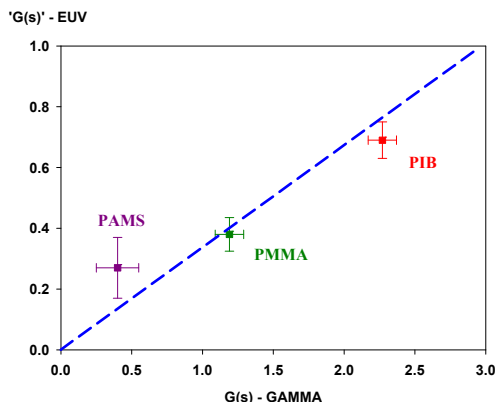
Figure 1. Relationship between the yields of products (G-values) for poly(α-methyl styrene), poly(methyl methacrylate) and poly(isobutylene).

As reported previously [1] we have determined the radiochemical yields of chain scission events for several common scissioning polymers using both EUV and gamma photons. The yield of chain scission events per 100 eV of absorbed energy, known as the G-value, G(S), is determined from the decrease in molecular weight with increasing dose. Figure 1 above shows the relationship between G(S) at the two energies for poly(α-methyl styrene), poly(methyl methacrylate) and poly(isobutylene). For these three polymers there is a good correlation between the radiolysis yields for the two techniques. There are a number of possible reasons for the differences in absolute G-values, for example differences in absorbance cross-section at 100 eV, or an overestimation in the absorbed dose in the case of EUV; this needs further investigation. Nonetheless, the relative sensitivities of the polymers remain the same for both types of irradiation. These results demonstrate that the sensitivity of polymers at 1 MeV can, therefore, be used as a predictor of sensitivity at 92 eV. We routinely use this method for final screening of polymers prior to EUV exposure.

3.2 Identification of Candidate Structures using MS Ionizer and QSPR Model

The above method of screening involves the laborious task of synthesizing a high polymer and measuring progressive changes in molecular weight on exposure. Our chemical knowledge however allows us often to predict, to a first approximation, the relative sensitivity of materials based on their chemical structures. However, for more complex structures, and those new to radiation chemistry, a more rigorous approach is needed. We have postulated [1] that the sensitivity to fragmentation of molecules in the ionization chamber (the impact energy of the electron ionizer is around 70 eV) of a GC-MS is proportional to the overall scission yield in a EUV source. A measure of the sensitivity is the ratio of the intensity of the parent ion signal to the total ion count (RMI, a parameter which decreases with increasing sensitivity to bond cleavage). Using this approach we have screened a very large number of small molecules for high sensitivity, and a summary of the results is shown below in Figure 2. The results show that candidate structures include ester, carbonates and sulfones, and that rejected structures are disulfides, amides aromatics and compounds containing conjugated double bonds.

Figure 3 shows the relationship between the experimental values of the RMI and those calculated from the QSPR model developed by us. As indicated above, a low RMI is an identifier of high sensitivity to ionization. The data points enclosed within the shaded ellipse in Figure 3 include molecules with those structures identified above, and in addition highly-branched structures, molecules containing electron withdrawing groups and halogenated compounds. Note that the model does not discriminate between these groups to high precision; to do so a model developed using data collected using a lower ionization energy would be required.
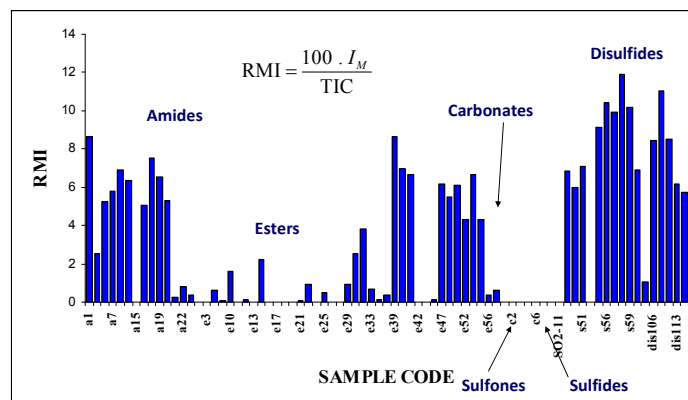
Figure 2. Results of GC-MS screening, with chemicals screened grouped according to chemical class.
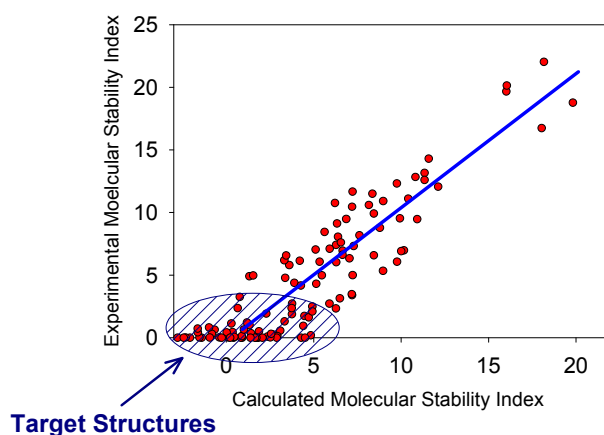
$$RMI = \frac{100 \cdot I_M}{TIC}$$

Target Structures

Figure 3. QSPR model derived from measurements of the RMI by GC-MS. The points enclosed in the ellipse are candidate structures.

3.3 Linear Polycarbonates

As indicated above the QSPR model developed by us has allowed us to identify structures of high sensitivity to ~100 eV photons. These include a range of carbonate-containing polymers. Aliphatic polycarbonates are characterized generally by their low glass transition temperature, and would be expected to exhibit low etch resistance. To overcome this we have introduced the concept of "hot-spot" polymers, in which EUV-sensitive groups bridge polymeric blocks which will impart higher glass transition temperatures and superior etch resistance. This concept is illustrated in Figure 4.
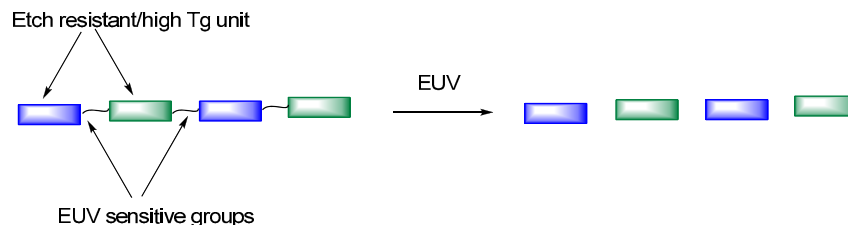
Figure 4. This figure illustrates the concept of hot-spot polymers. Highly EUV-sensitive groups are alternated with blocks having properties to impart high Tg, etch resistance, etc.

To identify highly-sensitive structures we have prepared a range of polycarbonates with secondary-tertiary carbons adjacent to the carbonate linkage. These have been synthesized using condensation polymerization using bis(carbonylimidazolide)s as activating monomer using methods adapted from Frechet et al. [2-4]. An example of this approach is shown below in Figure 5. The structures, molecular weights and thermal properties of a number of materials

prepared by us are listed in Table 1. Note that in particular the introduction of the adamantly group in the main chain leads to substantial gains in the glass transition temperature of the material; we expect a corresponding gain in etch resistance. The polymers reported have the highest reported values of T_g for aliphatic linear polycarbonates.
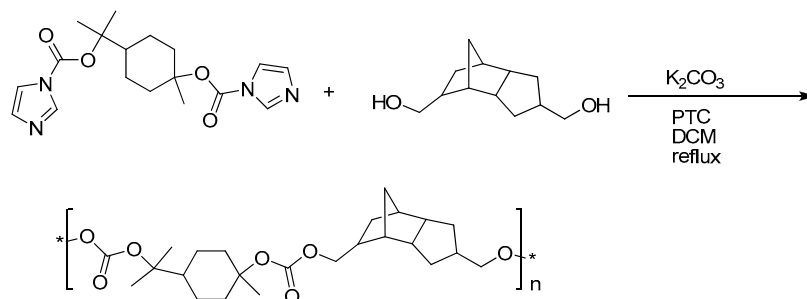

Figure 5. Example synthesis of polycarbonate using K_2CO_3 phase transfer catalyst.

Table 1. Structures and some properties of linear aliphatic polycarbonates.

Designation	Structure	MW	Tg (^{o}C)
PCIII		9620	126
PCIV		10270	97
PCVI		7600	49
PCVII		5120	92
PCVIII		4200	172
PCIX		11203	96
PCX		9100	63

3.4 Branched Polycarbonates

In this project we propose that higher sensitivity, a larger change in solubility for a given number of scission events, can be gained through linking property-modifying polymeric blocks to a highly-sensitive core or backbone. The concept is

illustrated in Figure 6 below in which in this simple example ring-opening polymerization is initiated from a trifunctional alcohol, resulting in a three-arm star molecule. The EUV-sensitive core can be extended by polymerization of blocks of for example methacrylate-based polymers using a method such as atom-transfer radical polymerization (ATRP).[5]
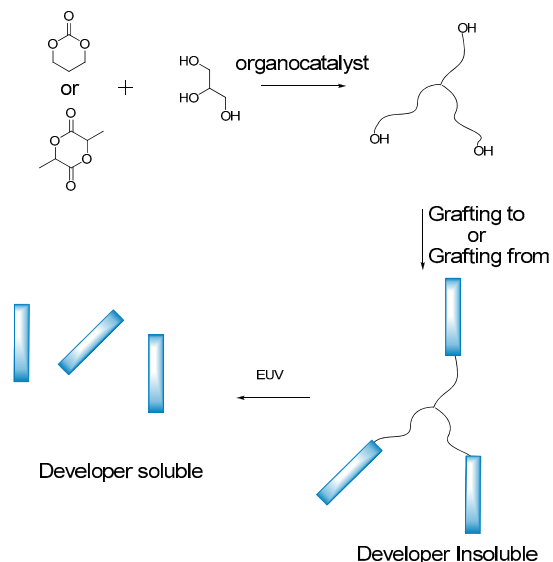
Figure 6. Schematic diagram showing structure of core-degradable star copolymers, the effect of EUV radiation on the tri-arm star polymer.

In a specific example (Figure 7), we have prepared six-arm poly(lactide) star polymers using an amine catalyst and sorbitol as the starting alcohol. Polymerization proceeds to high yield at 110 $^{\circ}$C. The hydroxyl end-groups can be subsequently converted to ATRP macro-initiator sites by conjugation to a bromo-isopropyl acid bromide.
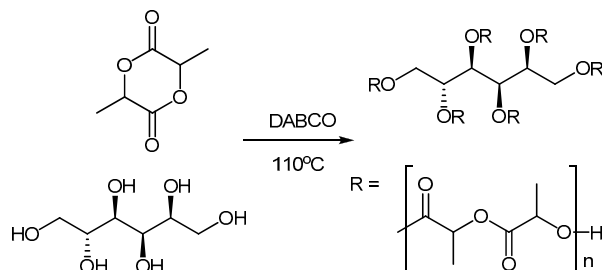
Figure 7. Polymerization of 6-arm star poly(l-lactide).
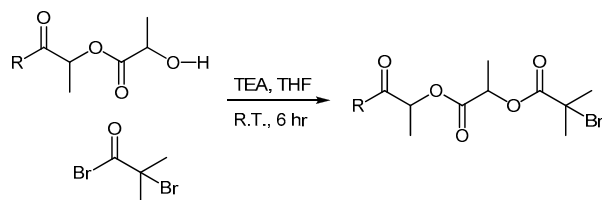
Figure 8. Functionalisation of hydroxyl end groups with BIBB to allow ATRP polymerization of methacrylate arms.

Figure 9 shows the ^{1}H NMR spectrum of a linear di-block copolymer which demonstrates that diblock copolymers of polyesters and methacrylate polymers are readily formed. The ^{1}H spectrum shows the characteristic peaks around 1 ppm due to the tacticity splittings of the alpha-methyl protons and a peak above 3.5 ppm due to the methoxyl protons of PMMA. The methyl and methine protons of the PLLA block appear around 1.6 and 5.2 ppm.
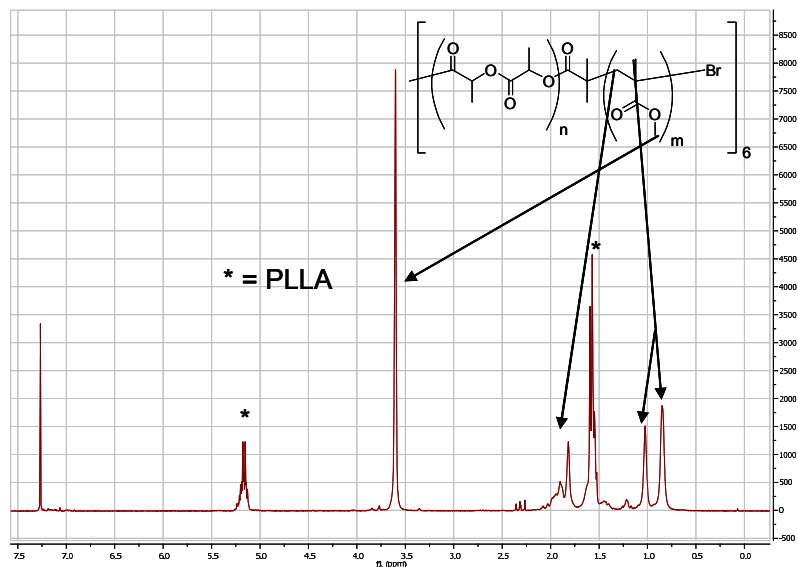
Figure 9. ^{1}H NMR spectrum of di-block copolymer of poly(l-lactide) and methyl methacrylate.

3.5 Polysulfones

In a final approach comb-type copolymers are being prepared by terpolymerisations of sulfur dioxide with an alkene and a macromer containing an alkene end-group. A similar approach has been reported by De Simone et al. [6, 7], however we are using controlled radical polymerization techniques to generate macromers, which allows significant diversity in the choice of monomers. The high sensitivity of polymer sulfones will impart high degradability to the main chain, while the comb chains arising from the alkene-functionalized macromers will impart the required mechanical and thermal properties to the final polymer. Aliphatic sulfones are well known for their sensitivity to high-energy photons.[8] They undergo rapid depolymerization due to their low ceiling temperature, T_c. The macromers will require a well-defined molecular weight such that when the comb polymer undergoes degradation, these units will be soluble in an appropriate developing solvent. The design approach is summarized in Figure 10.
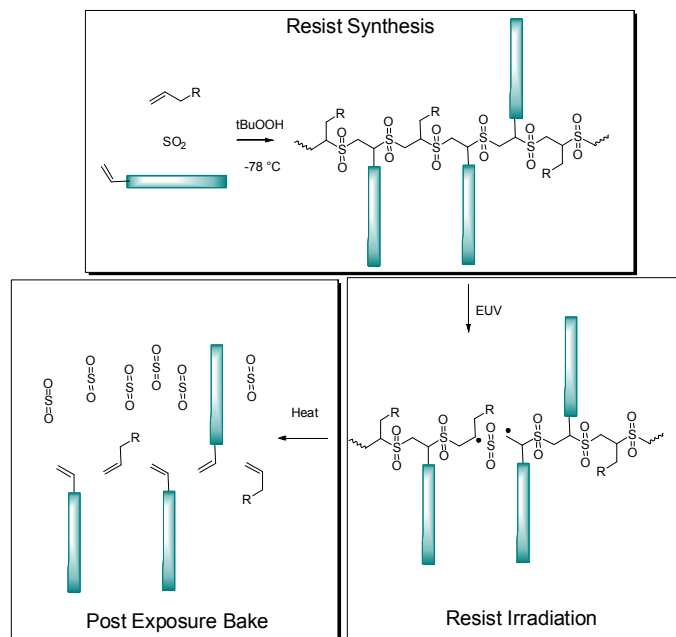

Figure 10. Schematic diagram showing structure of comb sulfone ter-polymers.

The alkene-terminal macromers were produced by ATRP of methyl methacrylate using an allyl-ether functionalized ATRP initiator (Figure 11). Target molecular weights of 2k and 5k were achieved with low polydispersity indexes. Terpolymers of sulfur dioxide, 1-pentene and the macromer were subsequently prepared by free radical polymerization at -78 °C using t-butyl hydrogen peroxide as initiator. The properties of the resultant polymers are listed in Table 2, and show that the rate of incorporation of the PMMA macromer is much lower than expected from the composition of the comonomer mixture, with for example 1.2 mol. % incorporation of PMMA-macromer with a starting composition containing 10 mol. % macromer. However, this corresponds to ~30 wt. % of the PMMA in the final terpolymer. We ascribe the reduced rate of incorporation of the macromer to steric effects and possibly lower reactivity of the allyl ether to copolymerization compared with the alpha-olefin.
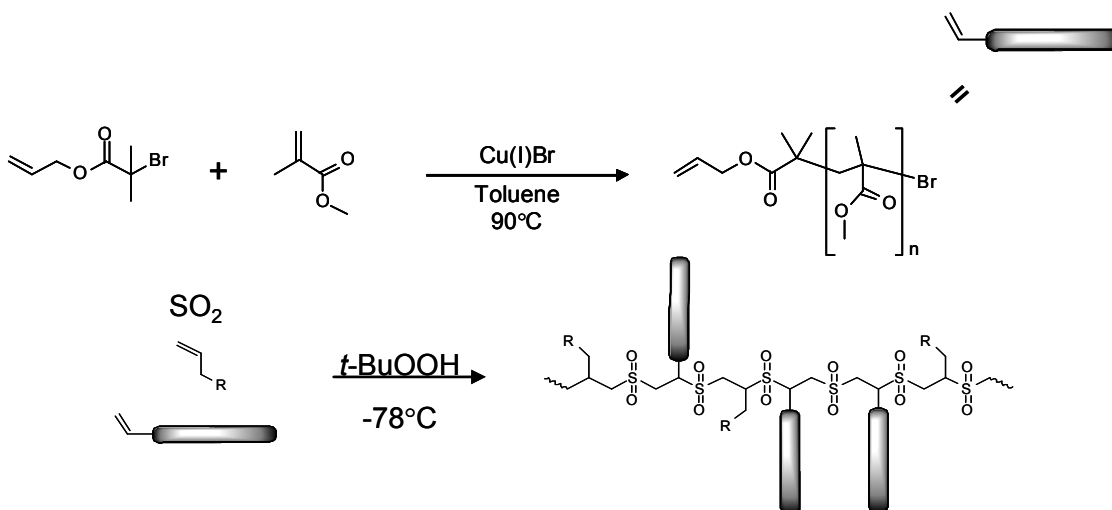
Figure 11. Preparation of methacrylate arms with allyl ether end group, and copolymerization with sulfur dioxide.

Table 2. Properties of methacrylate-sulfone comb copolymers.

PMMA feed %	Mn* (Da)	Mw/Mn	No. % PMMA in product	Wt. % PMMA in product	T_g (°C)
0%	431 400	2.36	-	-	85
1 %	494 600	2.28	0.1 %	0.3 %	84
2 %	312 900	1.66	0.2 %	1.18 %	84
10 %	128 800	1.49	1.17 %	29.3 %	84

3.6 EUV Exposures

Chemical contrast curves for PMMA, polysulfone-comb-PMMA and poly(1-pentene sulfone) are presented in Figure 12. PMMA exhibits only a very small decrease in thickness when exposed to 13 nm photons. In contrast both the linear polysulfone and comb polysulfone exhibit significant decreases in film thicknesses when exposed to 13 nm photons. The highest rate of loss occurs at doses less than 50 mJ cm^{-2}. These results show that polysulfones and very sensitive to 13 nm photons, which is consistent with the sensitivity of these polymers to other forms of ionizing radiation. The results also show that the comb architecture does not significantly retard the rate of degradation with 13 nm photons.
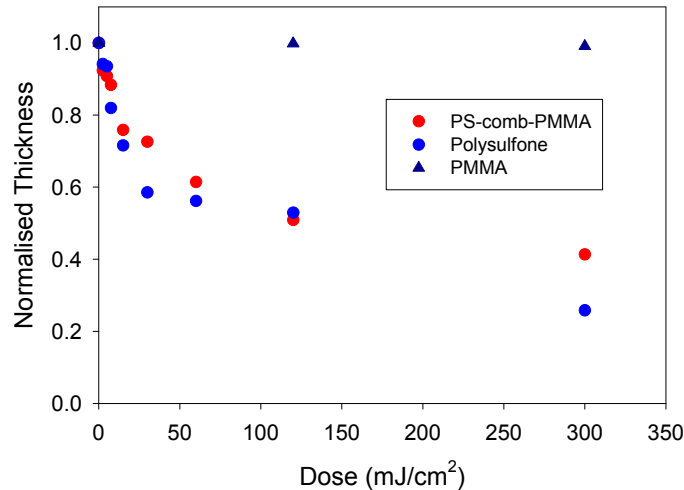
Figure 12. Normalized film thicknesses for three model systems, exposed at the Australian Synchrotron soft X-ray beam line.

Figure 13 shows some initial patterning results for star polycarbonate-*blk*-PMMA copolymers, linear polysulfones and comb polysulfones. The star polycarbonate-blk-PMMA copolymers were patterned at 50 nm half pitch, where a CD of approximately 41 nm. Some deformation of the line shape can be observed, which is likely due to swelling of the polymer during solvent development. This may be alleviated by further optimizing the composition of the developer solution. Other than the deformations induced by solvent swelling during development the LER of the patterns qualitatively appears to be low. The linear polysulfone was patterned at a 35 nm half pitch, where a CD of approximately 40 nm was obtained. Qualitatively the LER can be seen to be low. The poor signal-to-noise of the image is due to the high sensitivity of the resist, which was found to degrade in the SEM. The comb polysulfone was patterned at a half pitch of 50 nm, where a CD of approximately 37 nm was obtained. Defects are apparent in this image. The cause of these defects is uncertain at this point as is being investigated further. These patterning results are only initial attempts and it is expected that further optimization of the irradiation and processing conditions will result in better quality patterns. For each of the three systems that have been patterned the E_0 value is up to an order of magnitude lower than that reported for PMMA non-CARs.[9]
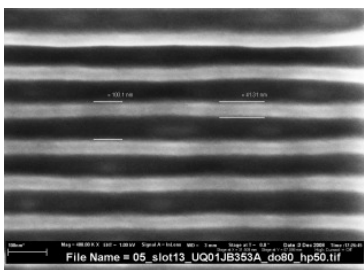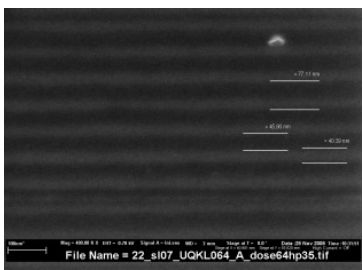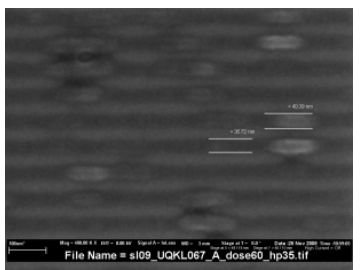
Star polycarbonate	Linear polysulfone	Comb polysulfone
hp 50 nm Dose to resist ~ 75 mJ/cm^2 CD ~ 41 nm	hp 35 nm Dose to resist ~ 35 mJ/cm^2 CD ~ 40 nm	hp 50 nm Dose to resist ~ 28 mJ/cm^2 CD ~ 37 nm

Figure 13. Results of patterning at 50 and 35 nm performed at PSI.

4. CONCLUSIONS

A range of linear aliphatic polycarbonates with high T_g have been synthesized. Star polycarbonate-block-PMMA copolymers and polysulfone-comb-PMMA have also been synthesized. Initial patterning results have been presented and although further optimization is required, at a qualitative level the LER for the systems appears low and significant reductions in E0 compared to PMMA have been observed.

5. ACKNOWLEDGEMENTS

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