# Modification Pathways for Copoly(2-oxazoline)s Enabling Their Application as Antireflective Coatings in Photolithography

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Chromophore-functionalized copoly(2-oxazoline)s are successfully evaluated as bottom antireflective coatings (BARCs) in high-resolution photolithography. With respect to UV light sources used in photolithographic production routines, anthracene is chosen as a chromophore. For application as polymer in BARCs, the copolymer poly(2-ethyl-2-oxazolin)$_{45}$-*stat*-poly(2-dec-9'-enyl-2-oxazolin)$_{20}$-*stat*-poly(2-(3'-(1''-(anthracen-9-ylmethyl)-1'',2'',3''-triazol-4-yl)-propyl)-2-oxazolin)$_{35}$ can be synthesized by the Huisgen cycloaddition click reaction of the copolymer poly(2-ethyl-2-oxazolin)$_{45}$-*stat*-poly(2-dec-9'-enyl-2-oxazolin)$_{20}$-*stat*-poly(2-pent-4'-inyl-2-oxazolin)$_{35}$ and the corresponding azide-functionalized anthracenes. These copolymers can be crosslinked by the thermally induced thiol-ene reaction involving the unsaturated C=C bonds of the poly(2-dec-9'-enyl-2-oxazoline) repetition units and a multifunctional thiol as crosslinker. Tests of this BARC in a clean room under production conditions reveal a significant decrease of the swing-curve of a chemically amplified positive photoresist by more than 50%, hence significantly increasing the resolution of the photoresist.
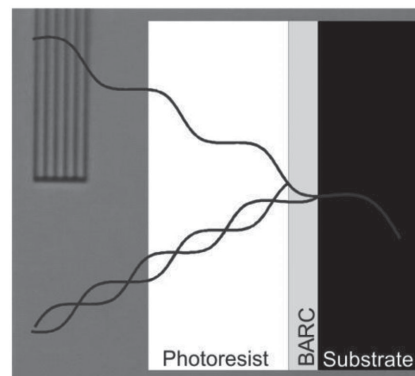
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1. Introduction

Photolithography is the most prevalent technique for the manufacturing of semiconductors or integrated circuits. The method commonly relies on the photochemically induced transformation of photoresists in order to change their solubility, which allows for the optical structuring of thin 2.5-dimensional patterns. The ongoing development of smaller, highly integrated and, in final consequence, more efficient electronic devices has depended on the development of high-resolution photoresists during the last decades.[1,2] As photolithography is based on optical principles, the smallest dimension that can be reproduced is dependent on the wavelength of the applied irradiation: Hence, the application of small wavelengths of the UV region is a key strategy for the reproduction of minimized structures with a high resolution.[3] Concomitant with the

decrease of feature sizes, the avoidance of reproduction errors has gained ever-growing importance.

Reproduction errors can, among others, be the result of the reflection of irradiation.[4] After passing the photoresist, the UV light is reflected on either the interface between air and the photoresist or on the interface between the substrate and the photoresist. In the latter case, the incident beam and the reflective beam interfere, which leads to standing waves and, hence, to a variation of the light intensity depending on the distance from the substrate, a so-called swing-curve of sinoidal shape.[5] This swing-curve is reproduced in the photoresist and significantly lowers its resolution, which can be quantified by means of the critical dimension, namely, the width of structures that can be reproduced by photolithography. In order to maintain high resolution of the photoresists despite standing waves, so-called bottom antireflective coatings (BARCs) may be applied between the substrate and the photoresist, in particular for photolithographic processes induced by UV light with wavelengths of 248 nm (KrF)[6] and 193 nm (ArF).[7] These BARCs are intended to decrease the intensity of the reflected beam by destructive interference and absorption.[8]

The basic requirements for polymer-based BARCs are (i) the solubility of the polymer and the crosslinker in low vapor pressure solvents, (ii) the ability of the material to absorb UV-radiation, (iii) sufficient adhesion of the material onto the substrate and the photoresist,[5,6] as well as (iv) the crosslinkability of the material (in order to avoid mixing of the components of the BARC and the photoresist).[9] As a rule-of-thumb, BARCs are required for resolutions of the dimension 0.35 µm (and lower), in which a BARC can reduce the swing-curve by more than 60%.[10] Notably, the adhesion of the photoresist on the BARC is a key parameter to ensure high resolution.[11]

This study focused on the application of functionalized and crosslinkable copoly(2-oxazoline)s as BARCs, motivated by the versatility of this polymer class that originates from the great number of differently substituted 2-oxazoline congeners, allowing for the synthesis of copolymers with tailor-made chemical functionalities.[12–14] While copoly(2-oxazoline)s can be obtained by the microwave-supported, cationic ring-opening polymerization,[15] numerous polymeranalogous reactions enable further functionalization of the copolymers,[16–22] including their application as negative photoresists.[17,20]

2. Experimental Section

All details of the Experimental Section have been summarized in the Supporting Information; the data of the copoly(2-oxazoline)s described in this study have been summarized in Table 1.

3. Results and Discussion

3.1. Modeling of the Swing-Curve of Polymer-Based BARCs

The light absorption of a polymer-based BARC depends on its absorption coefficient k and its refractive index n. The refractive index of a polymer can be altered within a small range only for a polymer class; the absorption coefficient, however, can be varied to large extent by changing the substitution pattern to the favor of chromophores. In order to estimate the targeted magnitude of the absorption coefficient of the poly(2-oxazoline)-based BARC to be designed, numeric simulations were performed with the aid of the s-litho software by synopsis/sentaurus, considering a stack of a silicon substrate, the antireflective polymer-based coating with the parameters n and k, and the chemically amplified poly(hydroxystyrene)-based positive photoresist M91Y (these modeled swing-curves have been represented in Figure 1, which also shows the experimental swing-curves).[23] The values for the parameters n and k were chosen based on the values in the range from 193 to 248 nm reported for two commercially available BARCs, namely, BCB of DOW Chemical and FLARE of Allied Signal.[24] The simulations show that the swing-curve oscillates with a wavelength of ≈70 nm, and that the targeted values of the absorption coefficient of the BARC material are in the range of $k = 0.3–0.5$.

3.2. Synthetic Strategy for the Preparation of Poly(2-Oxazoline)-Based BARCs

As a first design strategy for a poly(2-oxazoline)-based BARC material, a copoly(2-oxazoline) with olefinic substituents was chosen, namely, pEtOx$_a$-stat-pPhOx$_b$-stat-pDc=Ox$_c$ with a:b:c = 50:35:15 and 50:30:20. The olefinic functionalities of the Dc=Ox repetition units were considered reaction partners for thiol-functionalized chromophores in thiol-ene reactions as well as reaction partners during radical-induced crosslinking (Scheme 1). Therefore, a thiol-bearing anthracene derivative was synthesized via the reaction of 9-anthracene methanol with 1,5-dibromo pentane and the subsequent reaction of the obtained intermediate with hexamethyl disilathiane (Scheme 1). Column purification was required for the recovery of the product. Model studies of the functionalization of the copoly(2-oxazoline) with the chromophore (excluding the reaction with the crosslinker) by UV-induced thiol-ene reactions, however, revealed that a quantitative reaction could not be achieved within the preferred time window of 120 s. Even upon extended reaction times, the functionalization of the copolymer with the anthracene-chromophore did not go to completion (see the Supporting Information). Hence, simultaneous crosslinking

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■ *Table 1.* Composition and SEC data of the copoly(2-oxazoline)s described in this study.

Polymer name	Type and number of repetition units[a]						SEC data[b]	
	EtOx	Bu=Ox	Dc=Ox	Pen≡Ox	PhOx	Pr(Triaz-Anth)Ox	M_n [kDa]	$Đ_M$
pEtOx$_{50}$-*stat*-pPhOx$_{35}$-*stat*-pDc=Ox$_{15}$	52 (50)		15 (15)		35 (35)		6.6	1.73
pEtOx$_{50}$-*stat*-pPhOx$_{30}$-*stat*-pDc=Ox$_{20}$	50 (50)		20 (20)		31 (30)		5.8	1.92
pEtOx$_{70}$-*stat*-pBu=Ox$_{15}$-*stat*-pPen≡Ox$_{15}$	69 (70)	17 (15)		14 (15)			4.9	1.64
pEtOx$_{60}$-*stat*-pBu=Ox$_{15}$-*stat*-pPen≡Ox$_{25}$	60 (60)	16 (15)		24 (25)			5.0	1.71
pEtOx$_{45}$-*stat*-pDc=Ox$_{20}$-*stat*-pPen≡Ox$_{35}$	45 (45)		20 (20)	35 (35)			6.0	1.76
pEtOx$_{70}$-*stat*-pBu=Ox$_{15}$-*stat*-pPr(Triaz-Anth)Ox$_{15}$	70 (70)	15 (15)				15 (15)	5.4	1.78
pEtOx$_{60}$-*stat*-pBu=Ox$_{15}$-*stat*-pPr(Triaz-Anth)Ox$_{25}$	59 (60)	16 (15)				25 (25)	4.9	1.92
pEtOx$_{45}$-*stat*-pDc=Ox$_{20}$-*stat*-pPr(Triaz-Anth)Ox$_{35}$	45 (45)		20 (20)			35 (35)	6.3	2.24

[a]For each copoly(2-oxazoline), the experimental values (according to ^{1}H NMR analyses) as well as the targeted values are reported (the latter in parentheses); [b]As eluent, a mixture of chloroform/triethylamine/iso-propanol (94/4/2) was used at a flow rate of 1 mL min^{-1}. The results were referenced to polystyrene standards. For details, please see the Supporting Information.

and functionalization could not be completed at quantitative degrees. Considering the unfavored mixing of the components of the BARC, in particular the noncovalently bound chromophores, and the photoresist, which would lower the resolution of the photoresist,[25] a second design strategy needed to be developed.

Correspondingly, the covalent attachment of the chromophore to the polymer was performed prior to the crosslinking reaction (two-step strategy). For the functionalization of the copolymer with the chromophore, the azide-alkyne Huisgen cycloadditon click reaction was chosen. The application of the thiol-ene reaction for the crosslinking step was maintained. For the azide-alkyne coupling, 9-azidomethylanthracene was synthesized from 9-anthracenemethanol (Scheme 1). The synthesis could be performed in two steps, starting with the reaction of the reactant and thionyl chloride, followed by the reaction of the obtained chloride with sodium azide. This synthesis pathway proved to be a major advantage over the first strategy as extensive cleaning steps such as column chromatography were not required: The 9-azidomethyl anthracene could be recovered by liquid–liquid extraction. In order to provide reaction partners for these compounds, namely the azide and the (radical-induced) crosslinker, copoly(2-oxazoline)s of the compositions pEtOx$_a$-*stat*-pBu=Ox$_b$-*stat*-pPen≡Ox$_c$ (a:b:c = 70:15:15 and 60:15:25) and pEtOx$_a$-*stat*-pDc=Ox$_b$-*stat*-pPen≡Ox$_c$ (a:b:c = 45:20:35) were synthesized (Scheme 1). The Huisgen 1,3-cycloaddition could be performed under mild conditions at temperatures of 50 °C in orthogonal manner (with respect to the thiol-ene reaction or other radical-induced crosslinking strategies), preserving the olefinic moieties.

3.3. Ellipsometric Characterization of the Anthracene-Functionalized Copoly(2-Oxazoline)s

All types of copoly(2-oxazoline)s (Scheme 1) were used for the preparations of BARC formulations, using 1-methoxy-2-propanol as environmentally benign halogen-free solvent. Spincoating of the formulations was performed at 750 rpm in order to obtain layer heights of 130 nm. Pentaerythritol tetrakis (3-mercaptopropionate) was used as crosslinker after thermal induction: The formulations were coated onto silicone substrates (2 × 2 cm), dried at 80 °C, and heated up to 200 °C for 120 s in order to initiate the thiol-ene reactions for
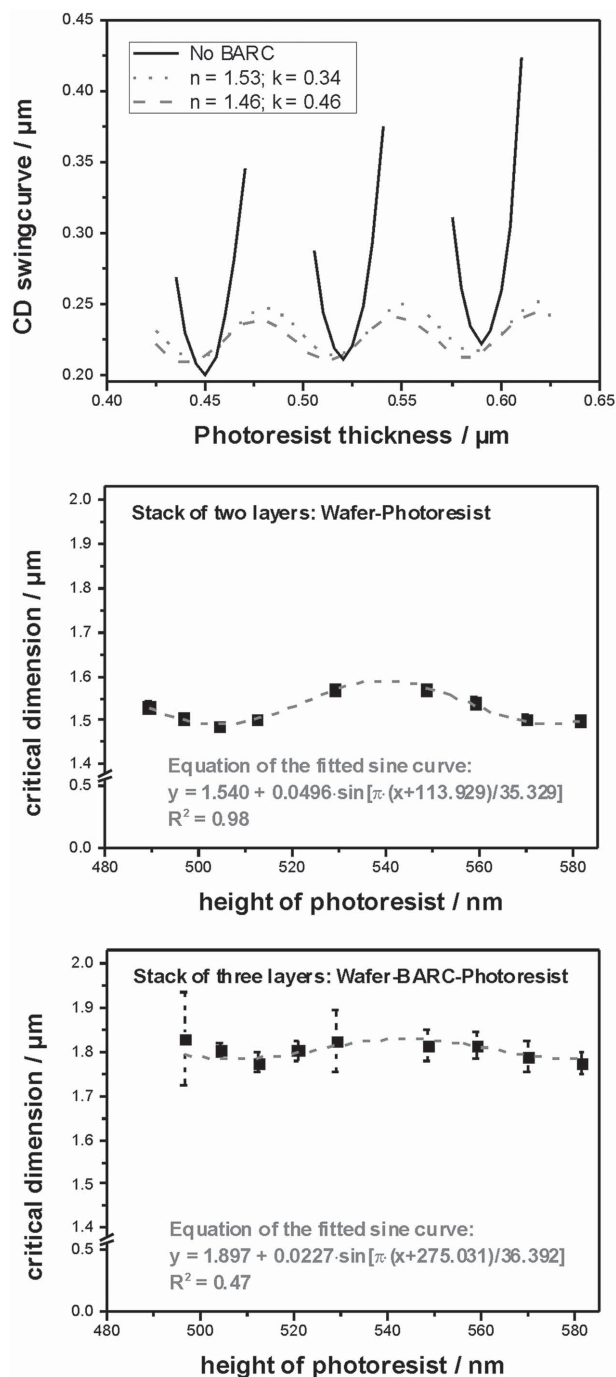
Figure 1. Top: Modeled swing-curves, considering a stack of substrate and photoresist M91Y (solid line) or a stack of substrate, BARC (with the refractive index *n* and the absorption coefficient *k*), and photoresist M91Y (dashed and dotted line). Middle and bottom: Swing-curves of the critical dimension of the photoresist without BARC (top) and with the BARC based on chromophore-functionalized pEtOx45-*stat*-pDc=Ox20-*stat*-pPr(Triaz-Anth)Ox35 (bottom). For comparison, both diagrams are drawn at the same scale.

crosslinking (and for functionalization with the chromophore in case of pEtOx$_a$-*stat*-pPhOx$_b$-*stat*-pDc=Ox$_c$). The refractive indices and absorption coefficients of layers composed of crosslinked chromophore-functionalized copoly(2-oxazoline)s (height: 130 nm), in correlation with the percentage of chromophore-functionalized repetition units, were determined at a wavelength of $\lambda = 248$ nm (considering photolithography of subsequent steps, based on the KrF wavelength) (Figure 2). Both, the refractive index n as well as the absorption coefficient *k*, show a sigmoidal correlation with the chromophore content. Notably, the presence of additional benzene groups of the repetition unit PhOx (in addition to the chromophor anthracene) or the variation of the repetition unit carrying olefinic functionality (pBu=Ox and pDc=Ox, respectively), did not significantly influence the refractive index or the absorption coefficient *k* for measurements at a wavelength of 248 nm.

3.4. Application of the Anthracene-Functionalized Copoly(2-Oxazoline)s as BARC

As the absorption coefficient *k* was identified as the most relevant criterion for antireflective behavior (Figure 1),[6,7] the copoly(2-oxazoline) pEtOx$_{45}$-*stat*-pDc=Ox$_{20}$-*stat*-pPr(Triaz-Anth)Ox$_{35}$ was chosen for application tests at clean room conditions. Due to the sigmoidal shape of the curves (Figure 2), a further increase of the chromophore content was not pursued for chromophore contents higher than 35%. For the application tests in a clean-room under process conditions, a BARC mixture of the copoly(2-oxazoline), the crosslinker pentaerythritol tetrakis (3-mercaptopropionate), and the initiator dicumyl peroxide was formulated in a mixture of 1-methoxy-2-propanol and ethyl lactate as solvent. The surface energy of this BARC after curing was found to be 47.85 ± 0.12 mN m^{-1}. The surface energy of pristine silicon wafers is 63.21 ± 0.09 mN m^{-1}, while that of tetraethyl orthosilicate- hexamethyl disilazane (TEOS-HMDS) silicon wafers is 48.14 ± 0.08 mN m^{-1}. The copoly(2-oxazoline)-based BARC showed good adhesion only on TEOS-HMDS wafers—adhesion on pristine silicon wafers as well as silicon wafers that were primed with HMDS was insufficient, indicated by the formation of comets and pinholes.

For the application of the BARC, a Cleantrack Act 8 spincoater and a Canon FPA 3000 EX6 step aligner were used. Thermal curing of the BARC was performed on a hot plate at 200 °C for 90 s. After the application and curing of the BARC formulation, the poly(hydroxy-styrene)-based photoresist M91Y was spincast.[23] Irradiation was applied by a KrF excimer laser with a dose of 220 mJ through a mask aiming at the reproduction of a geometric pattern after development in alkaline aqueous media. Swing-curves were recorded for (i) a set of wafers without the BARC (two-stack assembly of the wafer and the photoresist) and (ii) for a set of wafers with the BARC (three-stack assembly of the wafer, the BARC, and the photoresist).

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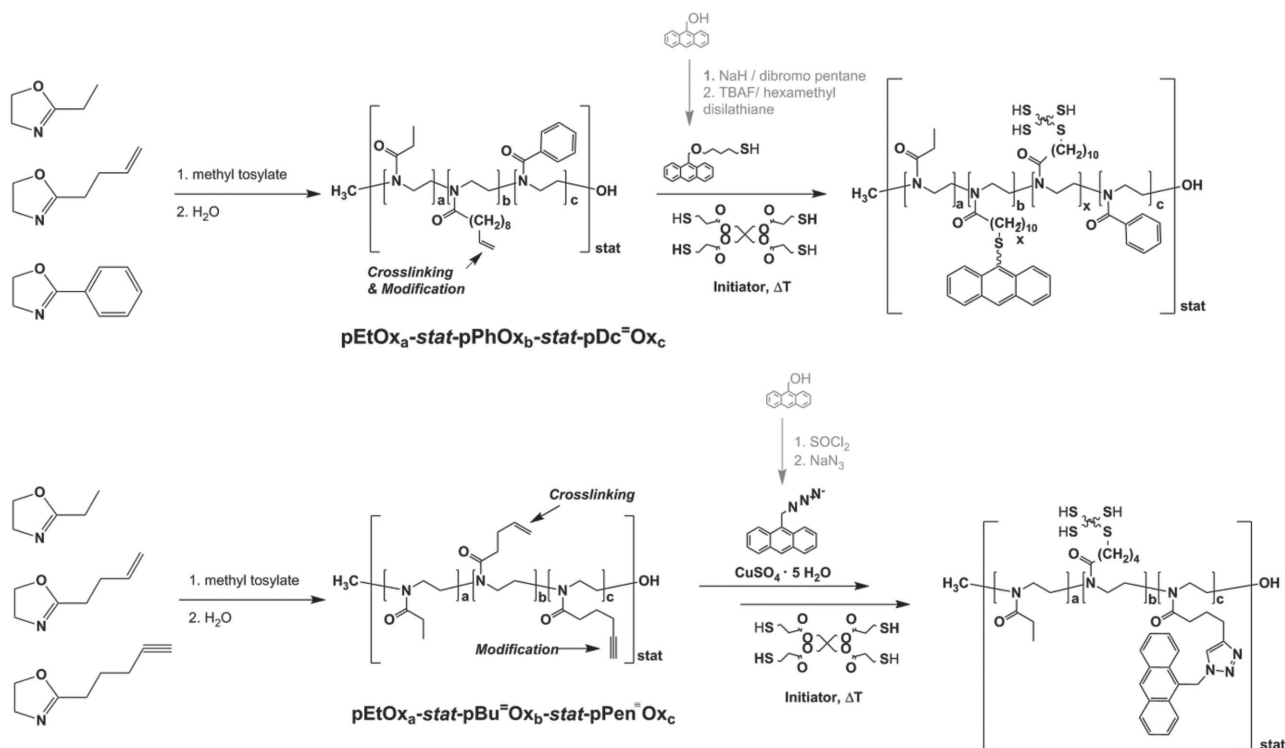
Scheme 1. Synthetic pathways for the synthesis of poly(2-oxazoline)-based BARCs. Top: Cationic ring-opening copolymerization of EtOx, Bu=Ox, and PhOx and subsequent simultaneous crosslinking and functionalization with anthracenes; the synthesis of the reactive chromophore is shown as an intersection. Bottom: Cationic ring-opening copolymerization of EtOx, Bu=Ox, and Pen≡Ox, functionalization of the copoly(2-oxazoline) with the 9-azidomethylanthracene chromophore(intersection) and subsequent crosslinking.

While the height of the BARC was unvaried at 80 nm, the height of the photoresist layer was increased systematically in the course of this study for each of the two sets of wafers.

Both series reveal a swing-curve (Figure 1) with a wavelength of ≈70 nm, which is in perfect agreement with the modeling data. Notably, the height difference (doubled amplitude) of the series without the BARC
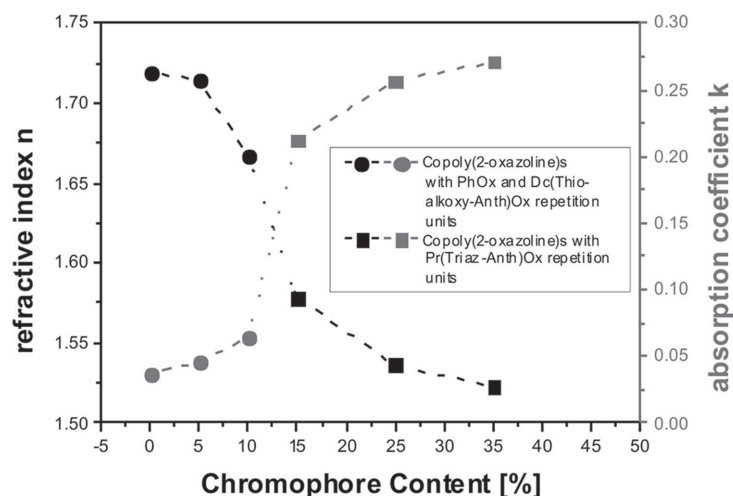
Chromophore content / % of repetition units	refractive index n	absorption coefficient k
0 [A]	1.7191	0.03706
5 [A]	1.7144	0.04516
10 [A]	1.6674	0.06467
15 [B]	1.5781	0.21246
25 [B]	1.5363	0.25681
35 [C]	1.5227	0.27087

Figure 2. Correlation of chromophore content and refractive index as well as absorption coefficient. The anthracene chromophore was present in the repetition units pDc(Thioalkoxy-Anth)Ox and pPr(Triaz-Anth)Ox. [A]: pEtOx$_a$-stat-pPhOx$_b$-stat-pDc=Ox$_c$-stat-pDc(Thioalkoxy-Anth)Ox$_d$ (a:b:c:d = 50:35,15:0, 50:35:10:5, and 50:30:10:10); [B]: pEtOx$_a$-stat-pBu=Ox$_b$-stat-pPr(Triaz-Anth)Ox$_c$ (a:b:c = 70:15:15 and 60:15:25); [C]: pEtOx$_a$-stat-pDc=Ox$_b$-stat-pPr(Triaz-Anth)Ox$_c$ (a:b:c = 45:20:35).

amounts to 99.2 nm, while that with the BARC exhibits a height of 45.4 nm. Hence, this copoly(2-oxazoline)-based BARC enhances the resolution of the photoresist by 55%, meeting common requirements of BARCs.[10] The different value ranges of the critical dimension in the range of 1.5 µm for the wafer-photoresist two-stack and the range of 1.8 µm for the wafer-BARC-photoresist originate from the fact that the light dose during photolithography was not adapted for the UV-light absorbing BARC layer and is further evidence of the light absorption by the BARC (Figure 1).

4. Conclusions

The BARC based on pEtOx$_{45}$-*stat*-pDc=Ox$_{20}$-*stat*-pPr(Triaz-Anth)Ox$_{35}$ significantly lowers the amplitude of the swing-curve of the commercially available photoresist M91Y by 55% and, hence, increases its resolution significantly under otherwise identical processing routines. A content of the chromophore anthracene of 35% (with respect to the repetition units) was found to be reasonably high, yielding a polymer with an absorption coefficient of $k = 0.271$. For the preparation of this copoly(2-oxazoline), the Huisgen cycloaddition (functionalization with the chromophore) and the thiol-ene (polymeranalogous crosslinking reaction) click reactions can be conveniently combined. For further optimization of this BARC, the addition of surfactants will be evaluated, aiming at increased reliability of the BARC by lowering the standard deviations of the critical dimensions.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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