

Laser Ablation of Arylazo Containing Polymers

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Abstract

New arylazo containing polymers (triazene, azophosphonate, alkoxy- and arylphosphorotriazene) specially designed for excimer laser ablation lithography were synthesized. Afterwards their behavior concerning excimer laser ablation was studied in several experiments. Applying the N-P or N-N coupling synthesis of bifunctional aromatic diazonium salt monomers with bifunctional phosphoric diesters or secondary amines, poly(arylazophosphonate)s and poly(triazene)s respectively can be easily prepared. The resulting polymers show excellent film forming properties and were exposed to a pulsed XeCl* excimer laser. The quality of the generated structures is demonstrated by Scanning Electron Microscopy (SEM) images. A new class of arylazo containing polymers poly(alkoxy-) and poly(arylphosphorotriazene)s was synthesized, as a combination of the arylazo chromophore with the phosphorous V element in the polymeric backbone. First results containing this new arylazo polymer class are presented in detail.

Keywords

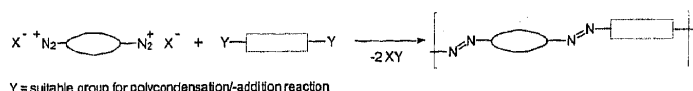
Laser ablation, microlithography, polymer, azo, phosphorous.

1. Introduction

UV-laser ablation is one of the most promising lithographic techniques for the microstructuring of polymer films. Laser ablation and the involved laser systems offer several advantages over conventional lithographic techniques¹⁻³. Polymers, which are suitable for laser ablation, should absorb the laser light and fragmentate into small molecular gaseous products. Moreover, it is helpful if the fragmentation is accompanied by formation of a driving gas, for example nitrogen. Therefore the polymers should contain photosensitive chromophores, which can be fragmented selectively.

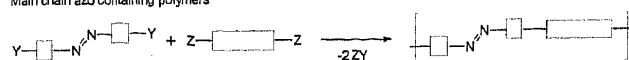
The preparation of new arylazo containing polymers useable for laser ablation can be realized with help of two main methods. In the direct pathway, a polycondensation reaction enables the azo chromophore and the polymer main chain to be formed simultaneously. The indirect method consists in the incorporation of the azo group within the monomer which is later on incorporated into a polymer (Figure 1).

Direct method



Indirect method

Main chain azo containing polymers



Side chain azo containing polymers

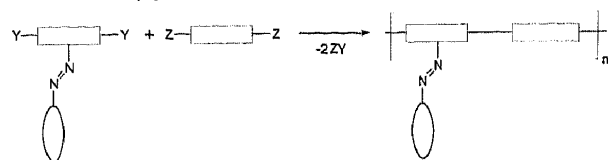


Figure 1 The direct and indirect method used to synthesize arylazo containing polymers.

After isolation, the polymer is processed into films of sufficient quality to be submitted to high resolution laser ablation. The phenomenon of ablation takes place when the material surface is irradiated by a pulsed laser.

A few nanoseconds⁴ after the laser irradiation, the photolabile group ($-N=N-X$) contained in these polymers (main or side chain) decomposes to give low molecular gaseous products. Material is etched away, ejected from the surface with supersonic velocity^{5,6}, leaving a two-dimensional pattern. Its geometry is defined by the masked laser beam (Figure 2). The hole depth can be controlled by the pulse number or by the energy of the laser beam (measured as fluence in J/cm^2). In order to obtain highly sensitive materials, we designed arylazo containing polymers with absorption maxima matching the laser irradiation wavelengths (308 nm for a XeCl* excimer laser)⁷. Three classes of polymers have been proved to fulfill the requirements of this approach: poly(arylazophosphonate)s, poly(triazene)s, and poly(alkoxy-) or poly(arylphosphorotriazene)s.

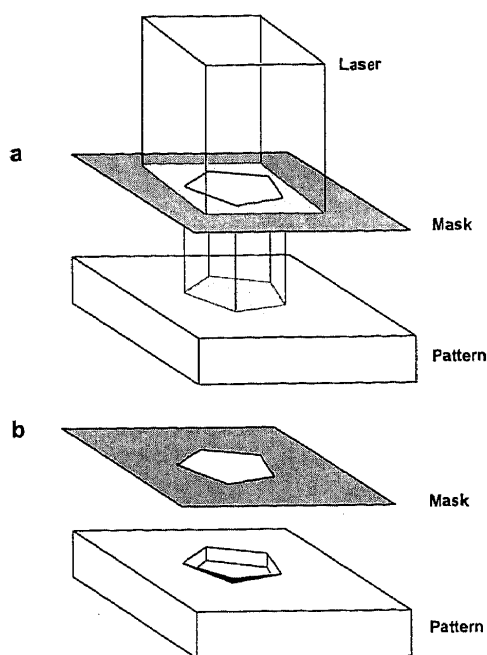


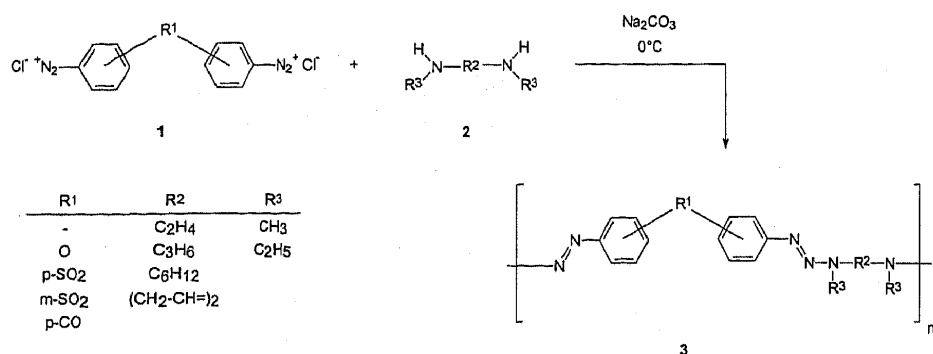
Figure 2 Laser ablation process.

2. Synthesis of azo containing polymers

2.1 Triazene containing polymers

Polymers containing 1-aryl-3,3-dialkyltriazene units in the main chain have been synthesized by several methods. The first preparation was realized by electrophilic N-N coupling of bifunctional aromatic diazonium salt monomers (**1**) and bifunctional secondary amines (**2**) (Scheme 1)⁸. Using this direct preparation pathway, the triazene chromophore and the backbone of the polymer were formed simultaneously by interfacial polycondensation. For this reaction, performed at 0°C, an aqueous solution of the bifunctional diazonium salt monomer was added to a mixture of chloroform/hexane containing the bifunctional amine in the presence of Na₂CO₃. After isolation and purification, polymers (**3**) in yields of 30–60% with molar masses up to $\bar{M}_n = 15400$ g/mol were obtained.

The resulting poly(triazene)s showed glass transition temperatures between 41 and 110°C and good thermal stability ($T_{dec} = 210\text{--}300^\circ\text{C}$)⁹. In a second step we modified that first synthetic approach developing a complementary indirect route. This new pathway consisted in synthesizing bifunctional triazene



Scheme 1 Direct preparation method for triazene containing polymers.

containing monomers which are then made to react in stoichiometric ratio with different comonomers. Choosing specific triazene containing monomers as well as suitable comonomers this new method allows to vary the architecture of the main chain and thus the polymer properties (e.g. glass transition temperatures) in order to adapt the triazene polymers to resist materials' requirements. One example of this indirect method is the reaction of bifunctional unsaturated triazene monomers (**4**) with dithiols (**5**) in the presence of AIBN in toluene at 55–60°C (Scheme 2)¹⁰. For this radical polyaddition a new monomer type (**4**) had to be synthesized by electrophilic N-N coupling of the diazonium salt of 3-aminostyrol with bifunctional amines in a 2:1 molar ratio in aqueous solution at 0–5°C in the presence of Na₂CO₃. The resulting polysulfides (**6**) were obtained in yields of 70% with molar masses up to $\bar{M}_n = 10400$ g/mol showing glass transition temperatures between –2 and 36°C and thermal stability up to 200°C.

The preparation of triazene containing polyesters (**9**) was achieved by polycondensation of triazene containing diols (**7**) with bifunctional acid chlorides (**8**) (Scheme 3)¹¹.

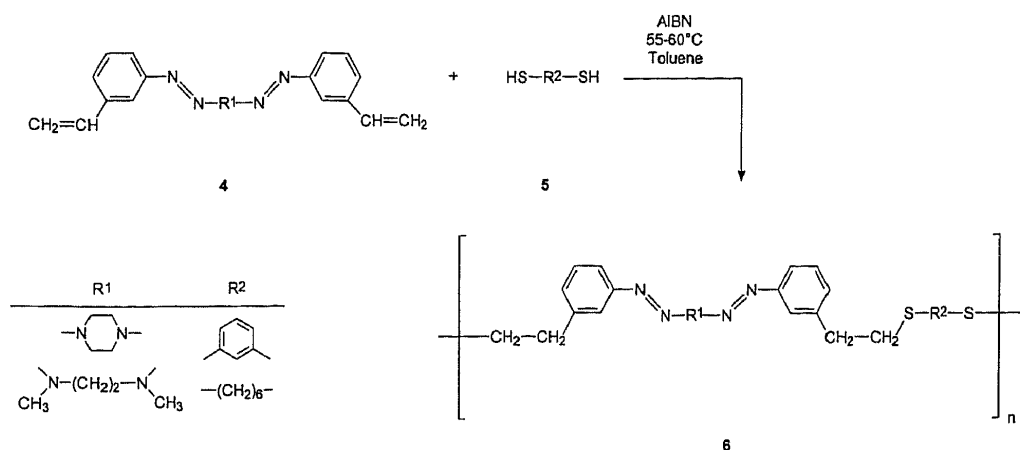
Aiming at bifunctional monomers with two hydroxy groups apart from the triazene chromophore a two step synthesis was elaborated starting with the electrophilic N-N coupling of the diazonium salt of ethyl-4-aminobenzoate with a bifunctional amine in a 2:1 molar ratio. The coupling was performed in aqueous solution at 0–5°C at pH > 8. The resulting bifunctional carboxylic ester was then reduced to the bifunctional benzylic alcohol (**7**) by means of LiAlH₄. 5-(*t*-Butyl)-isophthaloyl dichloride (**8**) was used as a diacyl monomer in order to obtain high glass transition temperatures (as a consequence of the increased rigidity of the polymer main chain). The resulting polyesters (**9**) were obtained in yields of 50–60% with molar masses up to $\bar{M}_n = 15000$ g/mol and showed good solubility in organic solvents such as tetrahydrofuran, chloroform and methylene chloride¹¹. The glass transition temperatures of the triazene containing polyesters ranged from 82 to 142°C; the thermal degradation of the polymers started at about 200°C.

Copolycondensation using an additional difunctional alcohol (1,4-bis(hydroxymethyl)benzene) as a comonomer led to copolyesters (CP X, X: % of triazene) with different contents of triazene in the main chain (according to Scheme 3)¹². The content of triazene was varied from 0–100% (CP 0–CP 100). Aiming at polymers with different topologies polyesters with triazene units in the side chain (**11**) were obtained according to Scheme 4 (CPS = **11**; R¹ = H).

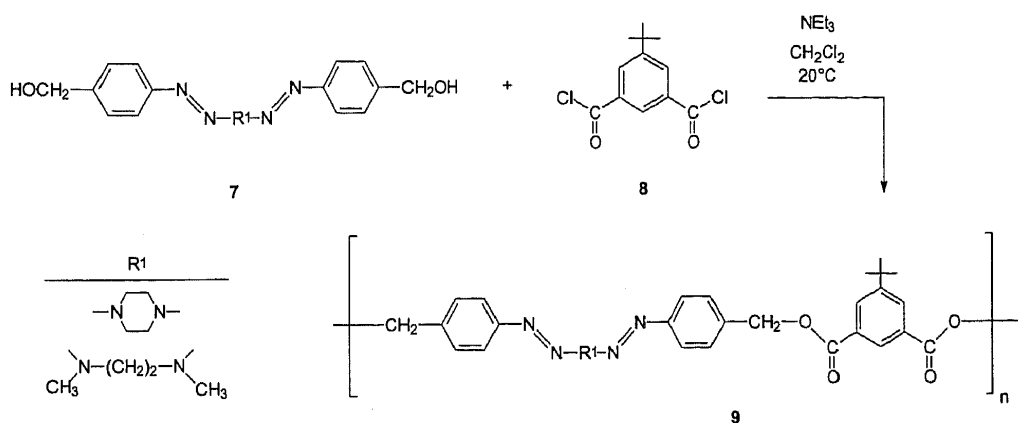
The reaction was performed at room temperature in methylene chloride as solvent. Triethylamine was added in order to neutralize the hydrochloric acid released during the condensation reaction. The resulting polyesters (**11**) were obtained in yields of 50–60% with molar masses up to $\bar{M}_n = 10000$ g/mol and thermal stability up to 140°C¹³.

Conclusion and outlook

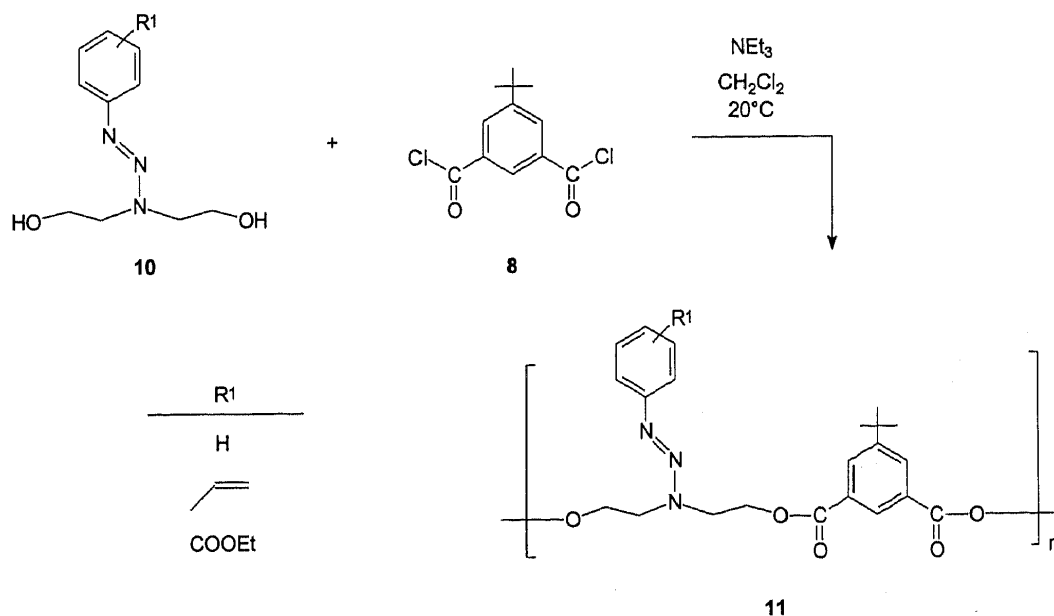
We developed two different preparation routes for polymers containing the 1-aryl-3,3-dialkyl unit in the main chain. Our recent investigations established the indirect



Scheme 2 Preparation of triazene containing polysulfides via radical polyaddition.



Scheme 3 Preparation of triazene containing polyesters via solution polycondensation.



Scheme 4 Preparation of polyesters containing triazene units in the side chain.

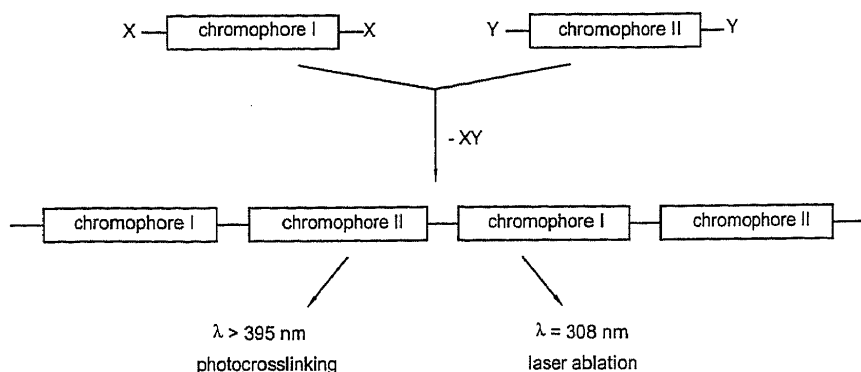


Figure 3 Indirect preparation method for photocrosslinkable triazene containing polymers.

preparation method as a convenient way to obtain a great variety of triazene containing polymers with different architectures and different thermal and photochemical properties. One of the outstanding features of triazene containing polymers is their good thermal stability. Their characteristic absorption between 290 and 350 nm due to the $\pi \rightarrow \pi^*$ conversion of the triazene chromophore make them excellently suitable for XeCl* excimer laser ablation.

Our present objective is to make polymeric triazenes available for applications in microelectronics or microlithography. For this purpose it is essential to create structures and thus polymers with mechanical and thermal stability as well as solvent resistance. This can be realized by incorporating photocrosslinkable units into the polymer backbone. In view of good quality and high stability of the micropatterns, the photocrosslinking units are activated selectively in a first step without destruction of the triazene units. In a second step the photocrosslinked material is structured by a pulsed XeCl* excimer laser. These specific requirements are met by using the indirect synthetic route, choosing bifunctional monomers, namely a triazene containing monomer (chromophore I) and a second photocrosslinkable monomer (chromophore II) which are then combined by polycondensation (Figure 3).

Due to their special photochemical properties the use of these materials as combined positive/negative resists for applications in microelectronics or microlithography is very promising.

2.2 Arylazophosphonate containing polymers

Polymers with arylazophosphonate units in the main chain can be synthesized via the direct or the indirect preparation method (Figure 1). The early arylazophosphonate containing polymers were prepared via the direct method by interfacial polycondensation¹⁴. Here the arylazophosphonate chromophore and the polymer backbone are formed during the polycondensation at the same time in a N-P coupling reaction¹⁵. The bifunctional phosphoric diester monomers (13) were synthesized according to the literature¹⁶. Through combination of various bifunctional diazonium salt monomers with different bifunctional phosphoric diester monomers, fifteen new polymers (14) were synthesized (Scheme 5).

For the interfacial polycondensation the bifunctional diazonium salt monomers (12) were prepared at 0°C in

aqueous solution and the bifunctional phosphoric diester monomers (13) were added as a solution in an organic solvent (tetrachloromethane or toluene). The N-P coupling reaction was started by addition of the base triethylamine. After isolation and purification, the polymers were obtained in yields from 26 to 85% with molar masses \bar{M}_n up to 15500 g/mol.

The thermal stability of the poly(arylazophosphonate)s was investigated by means of DSC measurements. The nature of the linking unit R^3 has an influence on the glass transition temperature (T_g). Flexible linking units ($-(CH_2)_2-$, $-(CH_2)_6-$ or $-(CH_2)_2-O-(CH_2)_2-$) result in a lower T_g , between 20 and 40°C. In contrast, rigid linking units ($-CH_2-c-hex-CH_2-$ or $-CH_2-p-ph-CH_2-$) increase the T_g in the range of 50 to 60°C. The photochemical behavior of these polymers was investigated by means of

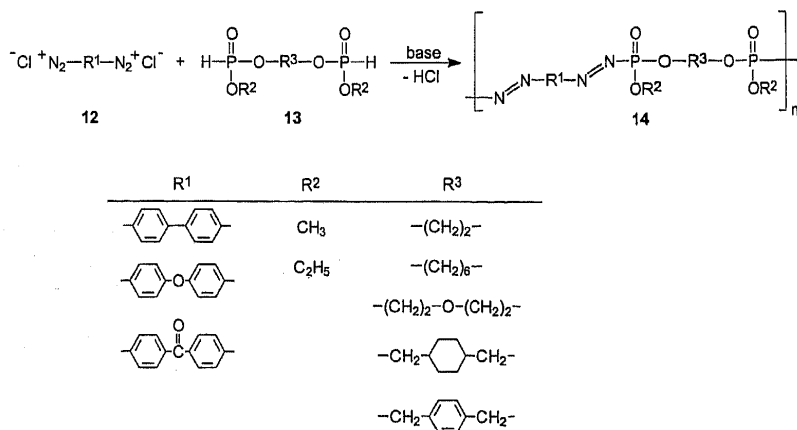
UV/VIS spectroscopy. All compounds show a characteristic absorption of the arylazophosphonate group between 303 and 356 nm making them suitable to laser ablation experiments.

For the indirect method a new monomer type was synthesized. Starting from bifunctional phosphoric diester compounds (15) in a common N-P coupling reaction several bifunctional arylazophosphonate diol monomers (17) were prepared (Scheme 6).

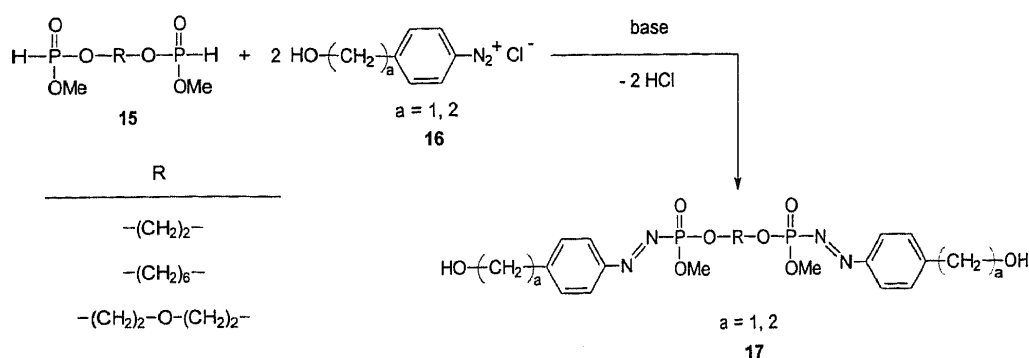
The versatility of the hydroxy group made it a candidate of choice for further polymerisation reactions. Indeed, first polyaddition experiments with common diisocyanate monomers (18) (hexamethylene diisocyanate, toluene-2,4-diisocyanate) were successful (Scheme 7). The polyaddition reaction was carried out in methylene chloride at 40°C with a catalytic amount of dibutyltin dilaurate¹⁷. The polyurethanes (19) were isolated in yields of 80% with molar masses (\bar{M}_n) from 3800 to 9900 g/mol.

DSC measurements show lower T_g 's for the aliphatic diisocyanate between 10 and 20°C. For the aromatic diisocyanate a remarkably high T_g of 60°C was determined. The UV/VIS spectroscopy revealed a characteristic absorption of arylazophosphonates between 298 and 310 nm for all arylazophosphonate containing polyurethanes.

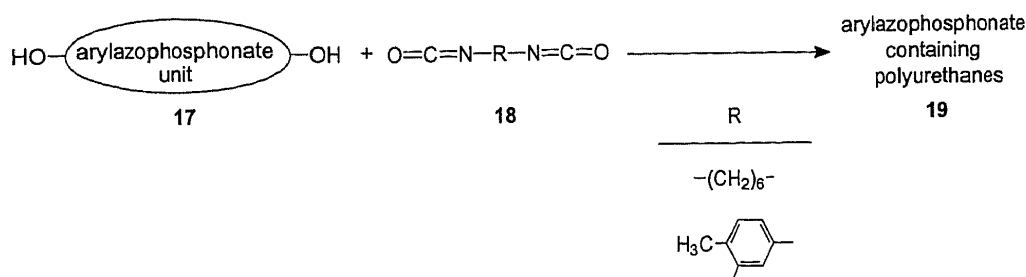
Furthermore, the bifunctional arylazophosphonate diol monomers (17) can be converted into arylazophosphonate containing polyesters (20) via polycondensation with a great



Scheme 5 Synthesis of poly(arylazophosphonate)s via interfacial polycondensation.



Scheme 6 Synthesis of new bifunctional arylazophosphonate diol monomers.



Scheme 7 Polyaddition of the bifunctional arylazophosphonate diol monomer with diisocyanate monomers.

variety of carbonyl monomers using coupling additives (e.g. EDC, DCC or CDI) analogous to common peptide coupling reactions (Scheme 8)¹⁸⁻²⁰. Because of the thermal decrease of the arylazophosphonate unit at temperatures about 150°C this route is preferred. Arylazophosphonate containing polyesters (20) can be obtained as well by using activated diester monomers²¹ (i.e. diphenylesters), for their excellent transesterification tendency at room temperature. However, the use of acid chlorides was excluded because of degradation side reactions involving hydrochloric acid released during the formation of the polyesters (even in presence of triethylamine or other bases).

Because of their absorption behavior between 303 and 356 nm poly(arylazophosphonate)s seem to be suitable materials for laser ablation experiments with commercially available XeCl* excimer lasers.

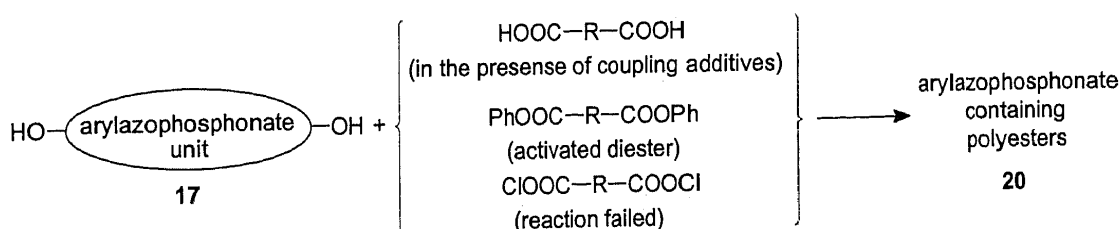
2.3 Poly(alkoxy-) and Poly(arylphosphorotriazene)s

As shown in the previous parts, the polymer families containing the azo group differ drastically in their physical properties and applicability. Triazene polymers are more thermostable than the poly(arylazophosphonate)s, in contrast the

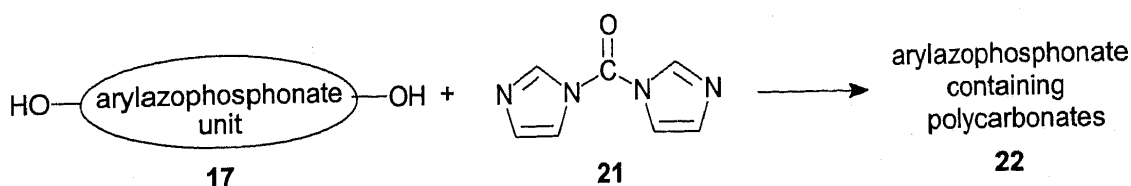
Furthermore, the diol monomers (17) can be converted into azophosphonate containing polycarbonates (22) with help of derivatives of carbonic acid (e.g. N,N'-carbonyldiimidazol (21)) (Scheme 9)^{22,23}. This new approach enables the synthesis of a new class of photosensitive polycarbonates containing arylazophosphonate units. The properties of these very promising polymer classes (polyesters/polycarbonates) are currently under study.

Conclusion

Polymers containing the arylazophosphonate unit were prepared easily with help of two different synthetic methods. Both direct and indirect method were used, nevertheless, the indirect method was proved to be more convenient for the synthesis of arylazophosphonate containing polyurethanes, polyesters, and polycarbonates polymers as high-quality materials for laser ablation.



Scheme 8 Synthesis of arylazophosphonate containing polyesters via coupling additives or activated diesters.



Scheme 9 Polycondensation reactions of bifunctional arylazophosphonate diol monomers to arylazophosphonate containing polycarbonates.

Feature Article

latter polymer class exhibits a higher photostability. Therefore the application of these polymers as photoresists²⁴ for photopatterning processes²⁵ depends on the experimental conditions. Worthy of interest appeared consequently the design and synthesis of a new class of azo containing polymers incorporating both the triazene function and the phosphorous V element. The synthesis of these new compounds and first results are presented below.

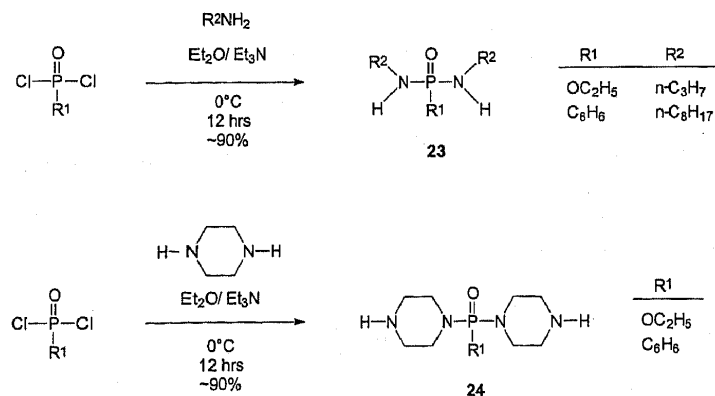
Monomer and polymer synthesis

The synthesis of the alkoxy- and arylphosphorodi(alkylaminate) monomers (monomer A and B) was achieved by a classic route (Scheme 10)²⁶. The phosphoric dichlorides were made to react with a primary amine in cooled ether (0°C) in the presence of a base (triethylamine). After filtration of the tertiary amine salt, the organic solutions were washed with water and dried over sodium sulfate. After removal of the solvent the phosphoric diamines were obtained in good yields (90%). Although fairly stable, the phosphoric diamines synthesized were found to degrade by reaction with water upon warming (90°C). A set of monomers for which the length of the amino alkyl chain, the nature of the amine function involved in the polycondensation reaction, as well as the substituent attached to the phosphorous nucleus, was easily prepared using this versatile reaction pathway. The monomers have all been characterized by the usual spectroscopic methods.

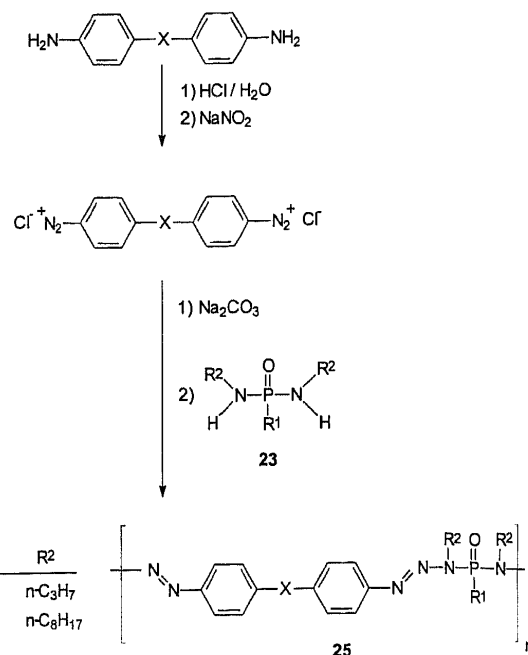
The synthesis of polymers containing the nitrogen atoms N-N in the backbone was performed by polycondensation reactions. The electrophilic N-N coupling is the chromophore-forming and backbone-building step and requires a bisdiazonium salt and a bifunctional amine (Scheme 11)^{8,27-29}.

Owing to their solubilities, the above mentioned components match the conditions required for interfacial polycondensation reactions, where the diffusion-controlled polyreaction occurs at an interface between an aqueous and an organic phase; however, the polymer precipitates immediately. In a first step, the aromatic diamine was diazotized in the presence of NaNO₂ in HCl/H₂O at 5°C, then treated with aqueous Na₂CO₃ until pH = 8–10. A solution of the phosphoric diamine in tetrachloromethane was added quickly at 0–5°C and the polymer precipitated readily upon further stirring as a red-brown solid. The polymers have been characterized using the conventional spectroscopic methods.

The molecular weights of the polymers thus obtained range



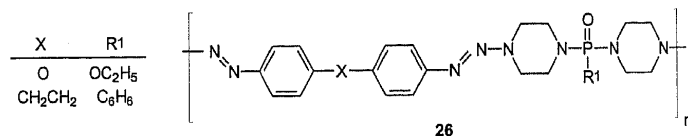
Scheme 10 Synthesis of monomer A (23) and monomer B (24) containing PV.



Scheme 11 Synthetic pathway to the alkoxy- and arylphosphorotriazene polymers (25).

between 2000 and 27000 g/mol (\bar{M}_n) and are comparable to those obtained after polycondensations carried out in homogeneous solutions. In contrast, the polydispersities of the obtained polymers are somewhat higher due to the diffusion-controlled interfacial reaction conditions (Table I).

Using the same procedure, a range of new polymers has been obtained from reaction with the monomer B (Scheme 12).



Scheme 12 Synthetic pathway leading to the polymers (26) presented in Table 1.

The results presented in Table I reveal how the choice of the monomers greatly influences the properties of the corresponding polymer. Thus, the polymers containing piperazine as R² tend to exhibit higher molar masses (\bar{M}_n), lower polydispersities (\bar{M}_w/\bar{M}_n) and increased solubilities (in DMF and CHCl₃) than the polymers with long alkyl chains as R². The influence of the substituent attached to the phosphorous nucleus (R¹) on the polymer properties is somewhat more difficult to disclose. The UV absorption spectra of these compounds display two large and non structured bands between 270 and 400 nm in DMF and in CHCl₃. These absorption bands were attributed to $\pi \rightarrow \pi^*$ transitions commonly observed for polytriazenes. Worthy to note is the bathochromic effect $\Delta\lambda \approx (10-30 \text{ nm})$ of the low energy transition (λ_2 in Table I) observed for the polymers containing the (P^V-N=N=N-Ph) repeating unit (25a–25h) compared to the more classical triazenes (P^V-N-Alkyl-N=N=N-Ph, 26a–26d). These strong shifts suggest a participation of the P^V moiety in the electronic states of the triazene chromophore as observed for

Table I Polymers obtained following Scheme 11 and 12. Variation of the structure (R¹, R² and X), yields, molecular weights, polydispersities, and maximum absorption wavelengths in CHCl₃.

polymer	X	R ¹	R ²	Yield (%)	\bar{M}_n (g/mol)	\bar{M}_w/\bar{M}_n	λ_1 (nm)	λ_2 (nm)
25a	O	OC ₂ H ₅	n-C ₈ H ₇	51	5 000	1.70	272	314
25b	O	C ₆ H ₆	n-C ₈ H ₇	29	3 500	2.08	272	348
25c	O	OC ₂ H ₅	n-C ₈ H ₁₇	11	2 000	4.11	272	340
25d	O	C ₆ H ₆	n-C ₈ H ₁₇	30	4 200	4.63	296	362
25e	CH ₂ CH ₂	OC ₂ H ₅	n-C ₈ H ₇	12	7 700	1.68	266	332
25f	CH ₂ CH ₂	C ₆ H ₆	n-C ₈ H ₇	23	6 100	2.36	289	354
25g	CH ₂ CH ₂	OC ₂ H ₅	n-C ₈ H ₁₇	43	4 300	3.15	284	346
25h	CH ₂ CH ₂	C ₆ H ₆	n-C ₈ H ₁₇	28	2 700	4.18	282	341
26a	O	OC ₂ H ₅	Piperazine	40	13 500	2.25	285	332
26b	O	C ₆ H ₆	Piperazine	72	28 600	1.94	296	324
26c	CH ₂ CH ₂	OC ₂ H ₅	Piperazine	85	25 200	2.22	296	320
26d	CH ₂ CH ₂	C ₆ H ₆	Piperazine	75	27 000	1.94	297	316

\bar{M}_n and \bar{M}_w/\bar{M}_n determined by means of GPC (eluent: DMF, standards: PS).

hexazadienes (Ph-N=N-N-N-N=N-Ph)²⁵. Further studies are currently undertaken in order to disclose the photochemical properties of these compounds (irradiation in solution and laser ablation) as well as their thermal stabilities.

Conclusion

A new class of polymers containing the photolabile group -N = N-X- in the backbone has been described. A versatile synthetic pathway allowed us to prepare a family of alkoxy- and aryl-phosphotriazene containing polymers possessing different physical properties. The absorption maximum of these new compounds makes them suitable for high resolution laser ablation experiments. Laser ablation experiments are to be carried out.

3. Ablation Experiments

Since the first reports of UV-laser ablation in 1982, many efforts have been undertaken to understand the phenomenon of laser ablation³⁰⁻³² and as well to develop new techniques, e.g. for arts restoration³³ or for microlithography³⁴⁻³⁶. In contrast to the conventional lithography, the wet developing step will be avoided due to the principle of ablation. Excimer lasers have been successfully used in structuring of polymers. Especially the XeCl* excimer laser emitting at wavelength of 308 nm is known for its high pulse energy and its pulse to pulse stability.

Basic studies for understanding the ablation mechanism were carried out with standard polymers such as polymethylmethacrylate (PMMA)^{37,38} or polyimide (PI)^{39,40}. Since most standard polymers do not exhibit an appreciable absorption at wavelengths above 300 nm, they are not suitable for structuring with a XeCl* excimer laser ($\lambda_{irr} = 308$ nm). An approach for structuring polymers with low absorption at the irradiation wavelength is doping the polymer matrix with chromophores^{24,41,42}. The progress in microelectronics increases the demand for resists which are suitable for short wavelengths to improve the resolution. Therefore a lot of work was spent to develop new photoresists based on azo groups suitable for excimer laser ablation lithography (EAL).

Since the azo group exhibits a strong maximum of absorption in the UV, this group is predestined as the functional unit in the backbone of the polymer chain. The azo group can fulfill three important functions for a successful dry etching resist: firstly, the

high absorption coefficient assures that the light energy will effectively be coupled into the material, secondly, after absorbing the light the azo group will decompose and break the polymer chain into small fragments, and thirdly, the released nitrogen will act as driving gas and support the removal of the fragments from the surface.

3.1 Experimental Methods

The azo group containing polymers were investigated with regard to their ablation behavior and resolution. In general, there exists a threshold for the applied laser energy fluence below which no ablation occurs, only a modification of the polymer surface takes place⁴³. At very high energies saturation is observed, and an increase in the energy deposited per surface area does not result in deeper structures. In the medium range

of energies the following equation was empirically found to be valid³². The etched depth per pulse (etch rate z) is proportional to the logarithm of the applied energy area density (fluence F). Two characteristic parameters (F_{th} : threshold fluence, α_{eff} : effective absorption coefficient) can be determined.

$$z(F) = \frac{1}{\alpha_{eff}} * \ln\left(\frac{F}{F_{th}}\right) \quad (1)$$

Thin films (20–100 μ m) have been prepared by casting from solution in tetrahydrofuran or chloroform onto glass substrates, and were dried in vacuo for several days. For determination of the ablation rates a pin hole mask was demagnified with a lens to a final size of 300 μ m in diameter, and the etched depths were measured with a mechanical profiler. For the high resolution experiments a structured mask was used and imaged with a reflection objective onto the sample to avoid spherical aberration. The experimental setup is described in detail elsewhere⁴⁴. The quality of the microstructures was investigated by scanning electron microscopy (SEM) and by atomic force microscopy (AFM).

3.2. Comparison of Ablation Characteristics⁴⁵

Triazene containing polymers

Triazene containing polymers exhibit a strong UV-absorption in the range from 290 to 380 nm depending on the substituent R₁. All the representatives of the poly(triazene)s exhibit nearly the same threshold fluence ($F_{th} \approx 100$ mJ) and comparably good microstructuring behavior as illustrated in Figure 4. It should be mentioned that the derived threshold fluence is dependent on the measurement method and the energy range investigated. In a study⁴⁶ that concentrated on a low fluence range, F_{th} was determined to lie between 20 mJ/cm² and 25 mJ/cm². Additional transmission measurements exhibited a dynamic absorption behavior⁴⁷: transmission increased by a factor of four during irradiation at 308 nm.

In a photochemical study⁴⁸, the influence of the photolability in solution of these photopolymers on the characteristic ablation parameters was investigated (Table II). No correlation between the molar absorption coefficient α and the effective absorption

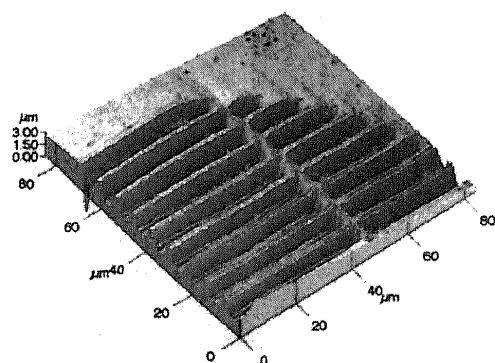


Figure 4 AFM-micrograph of polytriazene **3b** (1 pulse, 7.5 J/cm²).

Table II Substitution scheme and parameters of UV-ablation of the poly(triazene)s.

polytriazene	R ₁	R ₂	R ₃	qy [%]	F ₀ [mJ/cm ²]	α _{eff} [10 ⁴ · cm ⁻¹]	Z _{max} [μm/pulse]
3a	O	(CH ₂) ₆	CH ₃	0.26	104	1.83	3.2
3b	O	(CH ₂) ₂	CH ₃	0.39	96	2.2	2.7
3c	—	(CH ₂) ₆	CH ₃	0.17	117	1.85	2.8
3d	p-SO ₂	(CH ₂) ₆	CH ₃	0.12	104	2.19	2.6
3e	m-SO ₂	(CH ₂) ₆	CH ₃	0.16	80	2.29	2.4
3f	CO	(CH ₂) ₆	CH ₃	0.13	106	2.37	2.5
3g	O	(CH ₂) ₃	CH ₃	0.74	108	2.3	2.4
3h	O	(CH ₂ -CH=)	C ₂ H ₅	0.64	54	2.58	2.2
3i	CO	(CH ₂ -CH=)	C ₂ H ₅	0.16	129	2.31	2.4

coefficient α_{eff} was found, which is common for polymers under high energy irradiation⁴⁹. The etch rates of the poly(triazene)s **3a**, **3c–3f**, and **3i** increased with the quantum yield of photolysis at 308 nm, as expected for a photochemical decomposition pathway. In the subset of the oxygen bridged (R₁ = O) polymers (**3a**, **3b**, **3g**, and **3h**) a quite different behavior is observed: the polymers with the highest quantum yields show the lowest etch rates. This is explained by the following model: in the high energy regime a polymer with low photolysis quantum yield is capable of undergoing more cycles of photon absorption followed by thermalization, compared to the polymers with higher quantum yields. The fact that the product F_{th} · α_{eff} is not constant for all compounds is an indication for a photochemical decomposition process in comparison to a photothermal mechanism⁵⁰.

The results mentioned above suggest that in this group of polymers a photochemical decomposition mechanism during the UV-ablation dominates. According to the photochemical “two-level-model” for laser ablation presented by Pettit et al.⁵¹ the

relevant photochemical parameters have been determined and correlated. The results of ablation at two different UV-wavelengths (248 and 308 nm) could not be fitted to this photochemical model although it is known that the triazene containing polymers are very photolabile. The authors conclude that it is not possible to separate the ablation mechanism into a pure photochemical or photothermal pathway⁵². In another study⁵³ where the ablation process of triazene films was recorded and imaged with nanosecond interferometry it could be demonstrated by the swelling of surface that the ablation mechanism is influenced by both the photothermal and the photochemical pathway.

Triazene containing copolyesters

Triazene containing copolyesters (CP X, X: content of triazene in the main chain) have been investigated with respect to the influence of the content and position of the functional group (N=N-N)¹². It could be demonstrated that the breaking unit has to be placed into the main chain of the polymer to achieve sharp-edged structures. The copolyester with the triazene group in the side chain (CPS = **11**, R¹ = H) exhibits comparable etch rates (Table III), but in contrast to other compounds in this class the quality of the high resolution experiments showed a diminished resolution: the edges are rounded and the bottom is roughened. Experiments revealed that a minimum content of 35% of triazene in the main chain of these copolyester is necessary for sharp structures (Figure 7). Thermal damage impairs the achieved pattern quality of the polymers with a smaller percentage (Figure 5). On the other hand with a high content of triazenes another effect impairs the good ability of structuring this polyester: for > 90% triazene units in the backbone bubbles occur on the irradiated surface as can be seen in Figure 6. In contrast to other studies on polymer ablation^{41,54,55} no significant dependence of the characteristic parameters on the content of the chromophors was found despite the strong difference in the achieved structures. The results of this polymer group are summarized in Table III.

Usually, the ablation characteristics α_{eff} and F_{th} were found to be strongly dependent on the concentration of the chromophore. In doped^{24,41,42} and blended systems^{44,54,55} it was found that the threshold fluence and the limiting etch rates are decreasing with increasing dopant concentration. In a comparable study on polymer blends (polyester carbonates)⁴⁴ a local maximum of the etch rate was found depending on the dye concentration. The authors concluded that a minimum of polyester is necessary for ablation, but after this content of polyester is reached, the etch rates decrease due to the lowered penetration depths.

This phenomenon was not observed for the triazene containing copolyesters due to dynamic absorption behavior. Instead, a change of mechanism is proposed: at low concentrations a photothermal mechanism is prevailing, this can

Table III Parameters of UV-ablation of the triazene containing copolyesters.

content of triazene in %	CP 0 0	CP 1 1	CP 5 5	CP 20 20	CP 35 35	CP 50 50	CP 65 65	CP 75 75	CP 90 90	CP 100 100	CPS 100
α _{eff} [10 ⁴ · cm ⁻¹]	1.18	1.33	0.95	1.41	1.39	1.56	1.30	1.31	1.43	1.48	1.19
F _{th} [J · cm ⁻²]	0.60	0.50	0.69	0.22	0.26	0.28	0.37	0.34	0.32	0.33	0.54
z* [μm/pulse]	2.21	2.08	2.74	2.54	2.46	2.21	2.34	2.41	2.25	2.16	2.26

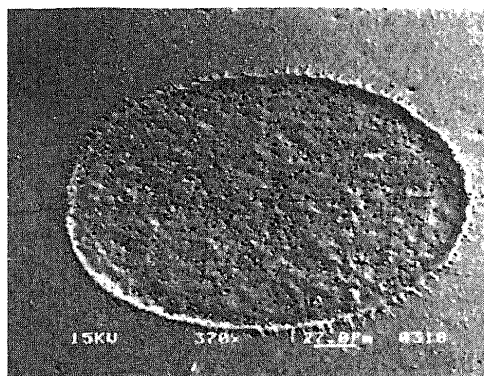


Figure 5 SEM-micrograph of CP 0 (1 pulse, 9.6 J/cm²).

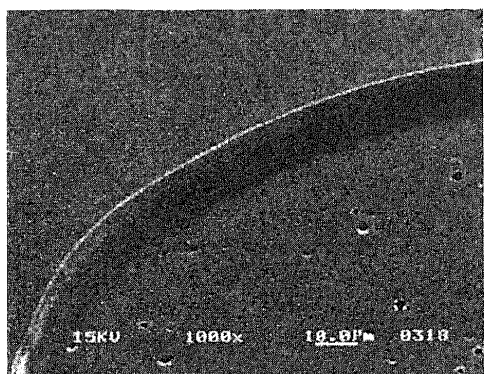


Figure 6 SEM-micrograph of CP 100 (14 pulses, 1.0 J/cm²).

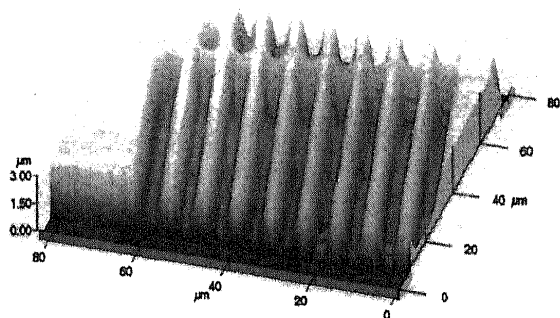


Figure 7 AFM-micrograph of CP 75 (1 pulse, 4.5 J/cm²).

be seen in the SEM-micrograph Figure 5: the bottom exhibits molten edges and rough bottoms. With increasing content of triazene a photochemical pathway is favored.

Poly(arylazophosphonate)s

Poly(arylazophosphonate)s are a newer class of arylazo containing polymers and have not been well characterized by ablation experiments. First results are summarized below. Poly(arylazophosphonate)s exhibit a UV-absorption band between 303 and 356 nm. In a photochemical study⁵⁶ it was demonstrated that this class exhibits a higher photostability than the investigated triazene containing polymers: quantum yields of

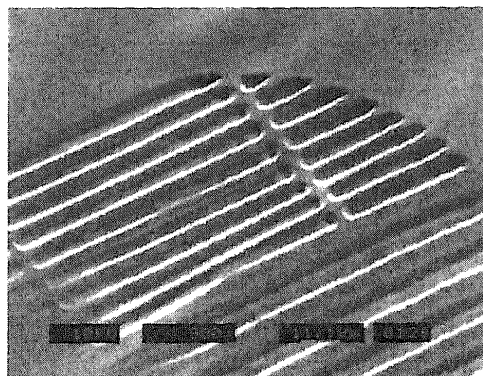


Figure 8 SEM-micrograph of test pattern 14e (1 pulse, 7.5 J/cm²).

Table IV UV-ablation parameters of the poly(arylazophosphonate)s.

poly(arylazo-phosphonate)s	R ₁ ^{a)}	R ₂	R ₃ ^{a),b)}	F _{th} [J/cm ²]	α _{eff} [10 ⁴ ·cm ⁻¹]	Z _{max} [μm/pulse]
14a	ph-ph	CH ₃	(CH ₂) ₆	1.16	0.97	—
14b	ph-O-ph	CH ₃	(CH ₂) ₆	0.89	1.08	—
14c	ph-O-ph	CH ₃	CH ₂ -c-hex-CH ₂	0.75	1.11	—
14d	ph-CO-ph	CH ₃	CH ₂ -c-hex-CH ₂	0.79	1.21	2.47
14e	ph-ph	CH ₃	(CH ₂) ₂ -O-(CH ₂) ₂	—	—	—

^{a)} ph = 1,4-disubstituted *p*-phenyl, ^{b)} c-hex = 1,4-disubstituted cyclohexyl (mixture of isomers: trans/cis=3/1)

photolysis at 308 nm in solution were determined to be as low as 0.2%. Despite their high photostability in solution the poly(arylazophosphonate)s show nearly the same etch rates as the triazene containing polymers. The quality of the structured pattern is excellent as is demonstrated in Figure 8. The pattern can clearly be seen without redeposited debris or damaged zones. The results of these polymers are summarized in Table IV. Further ablation experiments are currently under study.

3.3 Conclusion

Polymers containing arylazo chromophores as functional group for absorbing high energy UV-light are useful as photoresists for excimer laser ablation lithography. High resolution ablation could be achieved without any redeposited debris outside of the irradiated area. The ablation characteristics are similar for all investigated arylazo containing polymers (Table V). All polymers show appreciable etch rates combined with high resolution capability.

The main difference between the polymer classes are the stability towards atmosphere and light. The structured films of the triazene containing polymers did not exhibit any decomposition even after storage at room temperature under atmosphere for one year, whereas the poly(arylazophosphonate) films degraded within a few months.

For industrial applications, e.g. as photoresist for microelectronic devices (TFT-panels for portable computers³⁴), total removal of the polymer film from the substrate (e.g. Si-wafer) with fluences lower than 100 mJ/cm² is required for economic reasons. First experiments with the triazene polymers show promising results.

Table V Comparison of the ablation characteristics.

polymer class	λ_{\max} [nm]	$\varepsilon(\lambda_{\max})$ [l·mol ⁻¹ ·cm ⁻¹]	F_0 [J/cm ²]	α_{eff} [10 ⁴ ·cm ⁻¹]	Z_{\max} [μm/pulse]
poly(triazene)s	293–367	25700–38300	0.054–0.129	1.83–2.58	2.2–3.2
triazene containing copolyesters	293–316	–	0.33–0.69	1.18–1.48	1.4–2.7
poly(arylozo- phosphonate)s	305–360	–	0.75–1.16	0.97–1.21	2.5–3.0

4. Outlook

In this review we present a completely new and successful strategy to prepare highly efficient polymers for the excimer laser ablation lithography. It turned out that arylazo containing polymers bearing the photolabile arylazo moiety in the main chain are excellently suitable for high resolution micropatterning. The development of different synthesis pathways leading to these photolabile polymers allows to vary the physical properties of the resulting polymers in a wide range. Our present objective is to check the suitability of our polymers for various applications like microlithography, micromechanics etc. First experiments are already under study and show promising results.

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