Synthesis of Polymeric 1-Iminopyridinium Ylides as Photoreactive Polymers

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ABSTRACT: Two synthetic routes to polymeric 1-imino pyridinium ylides as new photoreactive polymeric architectures were investigated. In the first approach, polymerization of newly synthesized 1-imino pyridinium ylide containing monomers yielding their polymeric analogues was achieved by free radical polymerization. Alternatively, reactive precursor polymers were synthesized and converted into the respective 1-imino pyridinium ylide polymers by polymer analogous reactions on reactive precursor polymers. Quantitative conversion of the reactive groups was achieved with pentafluorophenyl ester containing polymers and newly synthesized photoreactive amines as well as by the reaction of poly(4-vinylbenzoyl azide) with a photoreactive alcohol. The polymers obtained by both routes were examined regarding their photoreaction products and kinetics in solution as well as in thin polymer films. Contact angle measurements of water on the polymer films before and after irradiation showed dramatic changes in the hydrophilicity of the polymers. © 2010 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 48: 832–844, 2010

KEYWORDS: change of hydrophilicity; functionalization of polymers; photochemistry; photoisomerization; polymer analogous reaction; radical polymerization; reactive polymers; stimuli responsive polymers

INTRODUCTION In recent years, much effort has been devoted to the synthesis of stimuli-responsive polymers for a broad variety of applications. Stimuli-responsive materials are able to change certain properties in response to specific external stimuli, such as temperature, pH, or light.[1–8] Among them, light represents an outstanding stimulus as it can be applied in a very precise manner by selecting suitable wavelengths, polarization directions, and intensities in a noncontact approach, respectively. In addition, light offers the opportunity to change the polymer properties in very confined spaces and, hence, can be used to create patterns in polymer thin films with nanometer precision, e.g., for potential use in optical data storage.[9–12] Regarding the photochemistry of polymers, light induced changes in solubility are of special interest.[13] Different photosensitive groups attached to a polymer backbone are known to alter their polarity by irradiation with light and, hence, influence the overall polymer solubility. As an example for the reversible change in polarity, spirobenzopyrane moieties undergo an isomerization process from the colorless closed spiro isomer to the open intensively colored merocyanine isomer under irradiation with UV-light.[14] This change is characterized by an increase in polarity and is completely reversible by thermal relaxation or irradiation with visible light.[14–16]

Irreversible transformation of polarity can be achieved by different approaches, whereby most of them include the detachment of a molecule fragment resulting in a polar moiety left on the polymer. Hereby, *o*-nitrobenzylic esters represent photocleavable groups which generate carboxylic acid moieties on the polymer backbone upon irradiation.[17,18] Furthermore, pyrenylmethyl ester side groups on polymers[19], 2-diazo-1,2-naphtoquinone (DNQ) based amphiphiles[20] and azido-functionalized polystyrenes[21,22] have been reported in the literature. Only little attention has been paid to the irreversible photochemical reaction of 1-imino pyridinium ylides, which is accompanied by a dramatic change in hydrophilicity without fragmentation of the molecule. As shown in Scheme 1, two reaction pathways compete in this photoreaction[23–27]: (a) The ring expansion via an excited singlet state leads to the corresponding 1,2-diazepines that exhibit a hydrophobic character and (b) the cleavage of the *N*—*N* bond under the detachment of pyridine via a triplet state leads to reactive nitrenes and isocyanato groups.

The ratio of diazepine formation versus *N*—*N* bond cleavage strongly depends on the substituent on the side of the carbonyl group opposite to the ylide nitrogen atoms. Heteroatoms, such as oxygen or nitrogen favor the diazepine

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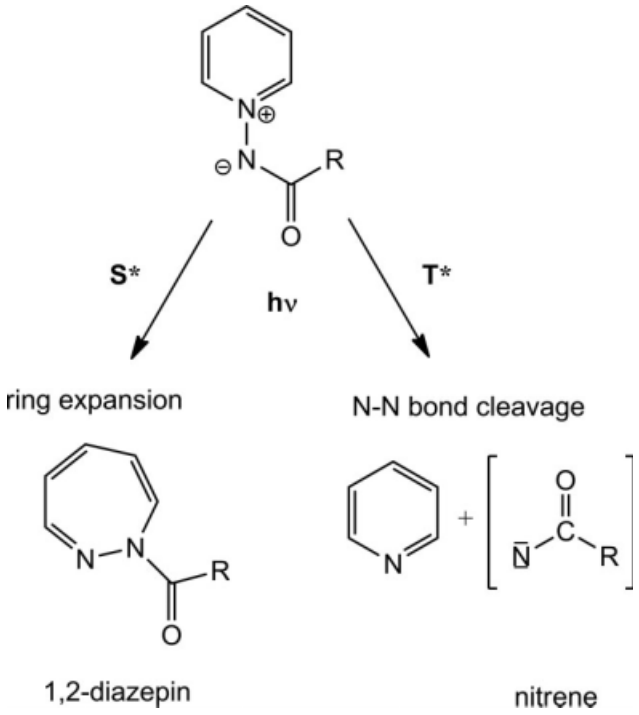


SCHEME 1 Photoreactions of 1-imino pyridinium ylides.

formation, while compounds with aliphatic substituents react mainly under pyridine elimination.[26,28,29] As such, the reaction pathway of ylides can be controlled by careful design of the chemistry. As mesoionic functionalities, 1-imino pyridinium ylides represent very hydrophilic groups, whereas the formed 1,2-diazepines are rather hydrophobic. In comparison the generated nitrenes or isocyanates may lead to further functionalization. On the basis of these considerations, polymeric 1-imino pyridinium ylides represent a very interesting class of photosensitive polymers, because their photoreaction can be tuned to yield either of the two different products resulting in different polymer properties.

Up to now, two different ways to synthesize polymeric 1-imino pyridinium ylides are known. Taylor et al.[30] presented the polymerization of a monomer based on the reaction of isocyanatoethyl methacrylate with 1-aminopyridinium ylide and investigated the photoreaction of the polymer and its potential use as an aqueous photoresist system. On the other hand, Kondo et al.[31] reported on the synthesis of polymeric pyridinium ylides by the reaction of poly(4-vinylpyridine) with a nitrene that was formed *in situ* by pyrolysis of ethyl azidoformate.

In general, the polymerization of functional monomers to yield high molecular weight polymers can be difficult. Therefore, alternative preparation routes utilizing reactive precursor polymers have been established. After synthesis of a reactive prepolymer, a big variety of functionalities can be introduced by polymer analogous reactions. Activated esters are well established in peptide chemistry[32] and the concept was successfully transferred to the preparation of reactive polymers.[33,34] Hereby, pentafluorophenyl esters are distinguished by their good solubility in a broad variety of organic solvents and their fast and quantitative reaction with amines at room temperature.[35–38] Additionally, for the reaction with alcohols as nucleophiles, poly(4-vinylbenzoyl azide) as an isocyanato groups generating polymer has recently been reported by our group.[39]

The aim of this work is the synthesis of novel 1-imino pyridinium ylide groups containing polymers. Two different synthetic pathways will be investigated and compared: (i) synthesis of new monomers containing 1-imino pyridinium ylide groups and their free radical polymerization, and (ii) synthesis of reactive precursor polymers and their conversion into polymeric 1-imino pyridinium ylides by reactions on the polymers.

EXPERIMENTAL

Materials

All chemicals were commercially available and used without further purification unless otherwise stated. Anhydrous THF and dioxane were distilled over sodium and benzophenone. $CHCl_3$ was dried over $CaCl_2$ and phosphorous pentoxide and freshly distilled before use. AIBN was recrystallized from diethylether. 4-Vinylbenzoylazide[39] as well as the activated ester monomers pentafluorophenyl methacrylate,[35] pentafluorophenyl acrylate,[36] and pentafluorophenyl 4-vinylbenzoate[37] were synthesized according to the literature.

Instrumentation

^1H and ^{19}F NMR spectra were measured using a Bruker AMX 300 at 300 MHz. FTIR measurements were performed using a Bruker Vector 22. UV-vis measurements were performed using a Shimadzu UV 2102 PC. GPC measurements were performed using tetrahydrofuran (THF) as eluant (flow rate = 1 mL/min) at 25 °C using a light scattering and RI detector. Polystyrene standards were used for calibration.

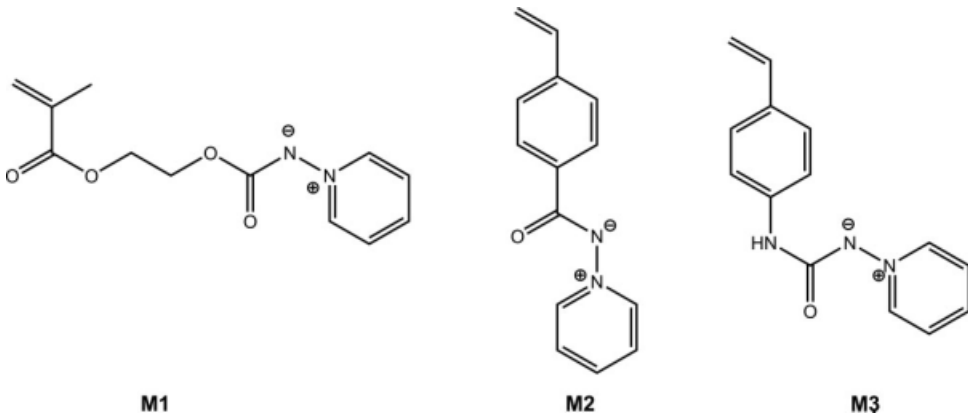
1-Aminopyridinium Iodide (1API)

The procedure of Gösl and Meuwsen [40] was followed. Briefly, three equivalents of pyridine were added to a freshly prepared solution of one equivalent hydroxylamine-*O*-sulfonic acid in cold water. After heating the mixture to 90 °C for 20 min and cooling it back down to room temperature, one equivalent of potassium carbonate was added. Water and excess pyridine were removed under reduced pressure and after the treatment of the residue with ethanol, the insoluble precipitate was removed by filtration. The reaction mixture was acidified with 57% hydroiodic acid. By storing the resulting solution for 1 h at −20 °C, yellowish needles separated. Recrystallization from ethanol yielded 70% of pure 1API as pink crystals. mp 160–161 °C.

^1H NMR (D_2O): $\delta = 8.73$ (d, $J = 6.6$ Hz, 2H), 8.35 (t, $J = 7.9$ Hz, 1H), 7.99 (t, $J = 7.4$ Hz, 2H), 4.79 (br s, 2H). ^{13}C NMR (D_2O): $\delta = 141.74, 140.14, 128.00$.

Synthesis of Monomers

The structures of the monomers M1, M2, and M3 are given in Scheme 2.



SCHEME 2 Photoreactive monomers based on 1-imino pyridinium ylides.

{[2-(Metacryloyloxy)ethoxy]carbonyl}(pyridinium-1-yl) azanide (M1)

A solution of hydroxyethyl methacrylate (HEMA) (2.60 g, 20.0 mmol) in THF (20 mL) was added dropwise to a stirred solution of carbonyldiimidazole (CDI) (3.36 g, 20.7 mmol) in anhydrous THF (50 mL). The reaction mixture was stirred for 4 h at room temperature and was added to a vigorously stirred suspension of 1API (5.00 g, 22.5 mmol) and potassium carbonate (25.00 g, 0.195 mol) in 50 mL of anhydrous THF. After stirring for additional 4 h, the inorganic salts were separated by filtration and the solvent was removed under reduced pressure. The deep blue residue was purified by column chromatography over silica using $CHCl_3$/MeOH (20:1) as eluant and yielded 95% of M1 (4.92 g, 19.7 mmol) as a yellow oil.

^{1}H NMR ($CDCl_3$): δ = 8.81 (d, J = 7.1 Hz, 2H), 7.79 (t, J = 7.2 Hz, 1H), 7.57 (t, J = 7.2 Hz, 2H), 6.12 (s, 1H), 5.52 (s, 1H), 4.40–4.30 (m, 4H), 1.91 (s, 3H). ^{13}C NMR (DMSO-d_6): δ = 166.64, 143.21, 137.46, 135.91, 126.83, 126 02, 63.75, 61.47, 18.11. MS (FD) *m/z* 250 (M^+). FTIR (cm^{-1}): 1717 (C=O), 1635 (C=O).

Pyridinium-1-yl-(4-vinylbenzoyl)azanide (M2)

A solution of 4-vinylbenzoic acid (6.00 g, 40.0 mmol) in THF (30 mL) was added dropwise to a stirred solution of CDI (6.62 g, 41.0 mmol) in anhydrous THF (80 mL). After the addition of 5 drops of triethylamine, the reaction mixture was stirred for 5 h at room temperature and was then added to a vigorously stirred suspension of 1API (9.83 g, 44.3 mmol) and potassium carbonate (48.00 g, 0.347 mol) in 50 mL of anhydrous THF. Stirring for additional 4 h was followed by removing the solvent under reduced pressure and the addition of 250 mL of $CHCl_3$ to the deep blue residue. The inorganic salts were separated and the remaining solution was reduced on a rotary evaporator. Purification of the residue was first done by column chromatography over silica using $CHCl_3$/MeOH (12:1) as an eluant and was followed by recrystallization of the obtained solid out of acetone. Seventy-four percent of M2 (6.67 g, 29.7 mmol) were obtained as yellow needles. mp 186 °C.

^{1}H NMR ($CDCl_3$): δ = 8.79 (d, J = 7.0 Hz, 2H), 8.09 (d, J = 8.3 Hz, 2H), 7.87 (t, J = 7.7 Hz, 1H), 7.63 (t, J = 7.2 Hz, 2H), 7.43 (d, J = 8.2 Hz, 2H), 6.74 (dd, J_{trans} = 17.6 Hz, J_{cis} = 10.9 Hz, 1H), 5.79 (d, J = 17.6 Hz, 1H), 5.26 (d, J = 10.9 Hz, 1H). ^{13}C NMR (DMSO-d_6): δ = 168.45, 143.51, 138.44, 138.22, 137.43, 136.57, 128.09, 126.75, 125.55, 114.97. MS (FD) *m/z* 224 (M^+). FTIR (cm^{-1}): 1580 (C=O).

Pyridinium-1-yl[(4-vinylphenyl)carbamoyl]azanide (M3)

4-Vinylbenzoyl azide (2.00 g, 11.5 mmol) was dissolved in 8 mL of anhydrous 1,4-dixoane and added dropwise under vigorous stirring to 20 mL of anhydrous 1,4-dioxane at 90—100 °C. The solution was stirred at this temperature for 3 h. The solvent was evaporated and the yellow oil of the isocyanate was dissolved in 10 mL of anhydrous acetone. Meanwhile, 1API (2.80 g, 12.6 mmol) together with potassium carbonate (14.00 g, 0.1013 mol) were grinded and suspended in 40 mL of anhydrous acetone. The suspension turned deep purple after 2 h of stirring at room temperature. The solution of the isocyanate was added dropwise under nitrogen atmosphere to the so prepared solution of the deprotonated 1API. After stirring for 3 h at room temperature, the inorganic solids were removed by filtration and the obtained deep blue colored solid was extracted three times with 250 mL of chloroform. The filtrates were combined and after evaporation of the solvents, the remaining solid was purified by column chromatography over silica using chloroform/methanol (5:1) as eluant. M3 (1.23 g, 5.1 mmol) was obtained in 44% yield after recrystallization out of acetone. mp 188 °C.

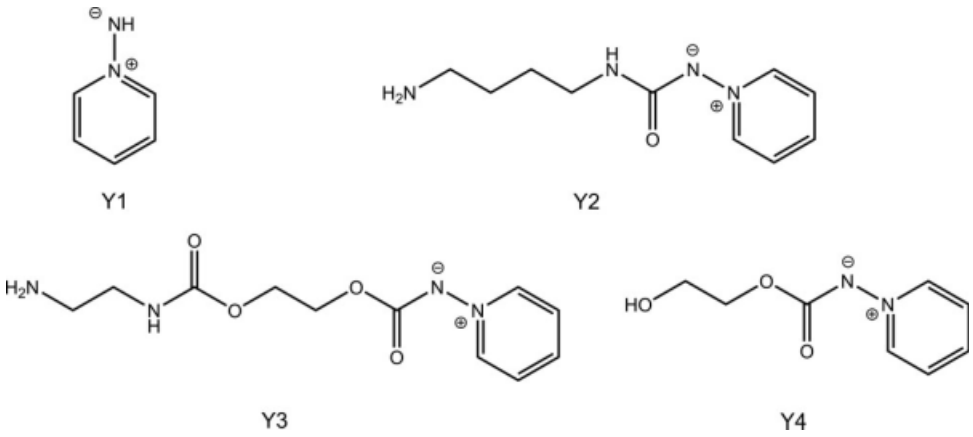
^{1}H NMR ($CDCl_3$): δ = 8.80 (d, J = 7.0 Hz, 2H), 7.74 (t, J = 7.7 Hz, 1H), 7.55 (t, J = 7.2 Hz, 2H), 7.41 (d, J = 8.7 Hz, 2H), 7.29 (d, J = 8.7 Hz, 2H), 6.63 (dd, J_{trans} = 17.6 Hz, J_{cis} = 10.9 Hz, 1H), 6.55 (br s, 1H), 5.59 (d, J = 17.6 Hz, 1H), 5.07 (d, J = 10.9 Hz, 1H). ^{13}C NMR (DMSO-d_6): δ = 161.64, 142.76, 142.68, 136.77, 135.59, 128.43 126.45, 126.41, 117.23, 110.44. MS (FD) *m/z* 239 (M^+). FTIR (cm^{-1}): 1621 (C=O), 1575 (N—H).

Synthesis of Functionalized 1-Imino Pyridinium Ylides

Four different ylides have been synthesized. The structures are presented in Scheme 3.

Y1

The free amine of 1API was generated *in situ* by stirring one equivalent of 1API with two equivalents of triethylamine in the respective solvent for 1 h at room temperature.



SCHEME 3 Amino- and hydroxy-functionalized pyridinium ylides for reactions on reactive precursor polymers.

[(2-Hydroxyethoxy)carbonyl](pyridinium-1-yl)azanide (Y4)
1API (10.00 g, 45.0 mmol) and potassium carbonate (50.00 g, 0.362 mol) were grinded and suspended in 90 mL of anhydrous THF. After stirring for 2 h at room temperature under nitrogen, the color turned deep blue. A solution of ethylene carbonate (4.05 g, 46.0 mmol) in THF (20 mL) was added dropwise to the suspension. The reaction mixture was stirred for 2 days at room temperature and for an additional day at 50 °C. The solvent was then evaporated and the deep blue residue was treated with 250 mL of chloroform. After filtration of the suspension, the solvent was removed under reduced pressure and the remaining blue solid was purified by column chromatography using methanol as eluant. Recrystallization of the so obtained red solid out of acetone yielded 66% of Y4 (5.38 g, 29.5 mmol) as yellow needles. mp 118 °C.

^{1}H NMR ($CDCl_3$): δ = 8.78 (d, J = 7.1 Hz, 2H), 7.82 (t, J = 7.7 Hz, 1H), 7.60 (t, J = 7.2 Hz, 2H), 4.25–4.20 (m, 2H), 3.82 (m, 2H), 3.42 (br s, 1H). ^{13}C NMR ($CDCl_3$): δ = 164.19, 142.73, 136.03, 126.13, 66.82, 62.37. MS (FD) m/z 182 (M^+). FTIR (cm^{-1}): 1635 (C═O), 1602 (*N*—H).

[(4-Aminobutyl)carbamoyl](pyridinium-1-yl)azanide (Y2)
A solution of *N*-BOC-1,4-diaminobutane (1.367 g, 7.26 mmol) in 5 mL of anhydrous THF was added dropwise to a stirred solution of CDI (1.193 g, 7.36 mmol) in 15 mL of anhydrous THF. The reaction mixture was stirred for 4 h at room temperature and was then added to a suspension of 1API (1.750 g, 7.88 mmol) and potassium carbonate (8.750 g, 63.31 mmol) in THF. After stirring the mixture for 4 h at room temperature and removing the solvent, the remaining deep blue solid was suspended for 1 h in chloroform. The insoluble inorganic salts were removed by filtration and the solvent was evaporated. For purification, column chromatography using methanol as eluant was followed by recrystallization from acetone. The obtained crystals were dissolved in deionized water and concentrated hydrochloric acid (9.58 g, 97.26 mmol) was added under cooling the solution in an ice bath. The mixture was heated slowly up to 50 °C and stirred for 20 h at this temperature. After the successful deprotection of the amino group, the mixture was cooled down to 2 °C and treated with potassium carbonate until pH ≈ 11. The water was removed under reduced pressure and the obtained beige solid was suspended for 1 h in anhydrous ethanol. The insoluble salts were removed and the solvent was evaporated. Y2 (0.652 g, 3.13 mmol) was obtained as an orange colored solid in 74% yield. mp 186 °C.

^{1}H NMR (MeOD-d_4): δ = 8.62 (d, J = 8.2 Hz, 2H), 8.14 (t, J = 7.8 Hz, 1H), 7.84 (t, J = 8.6 Hz, 2H), 3.23 (t, J = 6.7 Hz, 2H), 3.14 (t, J = 6.7 Hz, 1H), 2.70 (t, J = 6.9 Hz, 1H), 1.59 (s, 4H). ^{13}C NMR (MeOD-d_4): δ = 145.67, 139.18, 127.92, 42.38, 41.56, 31.37, 29.00. FT-IR (cm^{-1}): 1585 (C═O), 1470 (*N*—H).

[(2-{[(2-Aminoethyl)caramoyl]oxy}ethoxy)carbonyl](pyridinium-1-yl)azanide (Y3)
CDI (0.921 g, 5.57 mmol) was dissolved in 20 mL of anhydrous chloroform and a solution of Y4 (1.028 g, 5.64 mmol) in chloroform was added slowly. After 5 h of stirring at room temperature, the reaction mixture was added over a period of 1 h to a solution of 1,2-diaminobutane (0.518 g, 8.63 mmol) in the same solvent. The reaction mixture was stirred over night, the solvent was evaporated and the remaining solid was purified by column chromatography over silica using methanol as eluant. The product was obtained in 27% yield (0.403 g, 1.50 mmol) as a yellow-colored oil.

^{1}H NMR ($CDCl_3$): δ = 8.67 (d, J = 7.0 Hz, 2H), 7.73 (t, J = 7.7 Hz, 1H), 7.54 (t, J = 7.1 Hz, 2H), 6.31 (br t, J = 5.7 Hz, 1H), 4.13 (s, 4H), 3.04 (q, J = 5.9 Hz, 2H), 2.63 (t, J = 5.9 Hz, 2H), 1.90 (br s, 2H). ^{13}C NMR ($CDCl_3$): δ = 163.24, 156.81, 142.53, 135.66, 126.08, 63.59, 62.67, 43.82, 41.72. FTIR (cm^{-1}): 1706 (C═O), 1628 (C═O), 1538 (*N*—H).

Polymerizations
For all polymerizations, the monomers and 0.5 mol % of the respective initiator were solubilized in approximately 0.5 mL of the particular solvent for every 100 mg of monomer. The mixture was degassed by three freeze–thaw cycles and stirred under argon atmosphere for a predetermined polymerization time at a constant temperature. The polymerizations were terminated by rapid cooling and freezing. The homopolymers were purified by precipitation in a respective solvent. The crude polymers were dissolved in a good solvent, precipitated again, and finally dried in vacuum.

TABLE 1 Conditions of the Polymerizations of the Ylide Monomers M1, M2, and M3

Polymer	Monomer	Solvent	Initiator	T (°C)	t (h)	Precipitated In	Yield (%)
PM1	M1	NMP	AIBN	70	20	Acetone	87
PM2	M2	NMP	AIBN	70	42	Acetone	72
PM3	M3	NMP	AIBN	70	42	THF	14

Free Radical Polymerizations of the Photoreactive Monomers

Table 1 summarizes the synthetic details of the different reactions.

Free Radical Polymerization of M1

^{1}H NMR (DMSO-d_6): δ = 8.76 (br s, 2H); 8.01 (br s, 1H); 7.79 (br s, 2H); 4.10 (br s, 4H); 2.24–0.39 (br m, 5H). FTIR (cm^{-1}): 1725 (C=O), 1635 (C=O).

Free Radical Polymerization of M2

^{1}H NMR (DMSO-d_6): δ = 8.78 (br s, 2H); 8.03 (br s, 1H); 7.75 (br s, 4H); 6.66 (br s, 2H); 1.83 (br s, 3H). FTIR (cm^{-1}): 1672 (C=O).

Free Radical Polymerization of M3

^{1}H NMR (DMSO-d_6): δ = 8.79 (br s, 2H); 7.88 (br s, 1H); 7.70 (br s, 2H); 7.35 (br s, 2H); 6.60 (br s, 2H); 1.52 (br s, 3H). FTIR (cm^{-1}): 1632 (C=O), 1514 (*N*—H).

Free Radical Polymerizations of Activated Ester Monomers

Table 2 summarizes the synthetic details of the different reactions.

Free Radical Polymerization of Pentafluorophenyl Methacrylate (PFPMA)

^{1}H NMR ($CDCl_3$): δ = 2.71–1.89 (br m, 2H); 1.61–1.17 (br m, 3H). FTIR (cm^{-1}): 1776 (C=O). GPC (THF): M_n = 10,700 g/mol. M_w/M_n = 1.9.

Free Radical Polymerization of Pentafluorophenyl Acrylate (PFPA)

^{1}H NMR ($CDCl_3$): δ = 3.07 (br, 1H); 2.09 (br, 2H). FTIR (cm^{-1}): 1781 (C=O). GPC (THF): M_n = 3200 g/mol. M_w/M_n = 1.7.

Free Radical Polymerization of Pentafluorophenyl Vinylbenzoate (PFPVB)

^{1}H NMR ($CDCl_3$): δ = 8.03–7.57 (br, 2H); 6.96–6.35 (br, 2H); 2.26–1.12 (br, 3H). FTIR (cm^{-1}): 1760 (C=O). GPC (THF): M_n = 16,340 g/mol. M_w/M_n = 2.1.

Free Radical Polymerization of 4-Vinylbenzoyl Azide (4VBA)

^{1}H NMR ($CDCl_3$): δ = 7.61 (br s, 2H); 6.40 (br s, 2H); 1.75–1-14 (br m, 3H). FTIR (cm^{-1}): 2138 (N_3), 1688 (C=O). GPC (THF): M_n = 31,500 g/mol. M_w/M_n = 2.4.

Polymer Analogous Reactions

Polymer analogous reactions were carried out under nitrogen atmosphere in reaction tubes sealed with a rubber septum. The respective polymer was dissolved in a small amount of the appropriate solvent (Solvent 1) and added to the reaction tube. A solution of the functionalized pyridinium ylide in an appropriate solvent (Solvent 2) miscible with the solvent for the polymer (Solvent 1) was then added to the polymer solution. If necessary, the reaction phase was kept homogeneous by adjusting the solvent polarity by adding supplemental Solvent 2 in small portions. Conversion of the reactive groups was monitored by FTIR spectroscopy. After completion of the reaction, the polymer was precipitated, dissolved and precipitated again. For further purification size exclusion chromatography with Sephadex LH-20 as stationary phase was used. Scheme 4 shows the different reactions and Table 3 summarizes the synthetic details.

Polymer Analogous Reaction of PPFPMA with Y1 (PY1a)

^{1}H NMR (MeOD-d_4/dioxane-d_8 (3:4)): δ = 9.30–7.67 (br m, 5H); 3.26–0.86 (br m, 13.5 H).

Polymer Analogous Reaction of PPFPMA with Y2 (PY2a)

^{1}H NMR (MeOD-d_4/dioxane-d_8 (3:1)): δ = 8.66 (br s, 2H); 8.08 (br s, 1H); 7.82 (br s, 2H); 7.82 (br s, 2H); 3.23 (br s, 4H); 2.73–0.72 (br m, 18 H).

Polymer Analogous Reaction of PPFPMA with Y3 (PY3a)

^{1}H NMR (DMSO-d_6/MeOD-d_4 (7:1)): δ = 8.87 (br s, 2H); 8.04 (br s, 1H); 7.79 (br s, 2H); 7.25 (br s, 1H); 4.07 (br s, 5H); 3.04 (br s, 4H); 2.19–0.28 (br m, 6.1H).

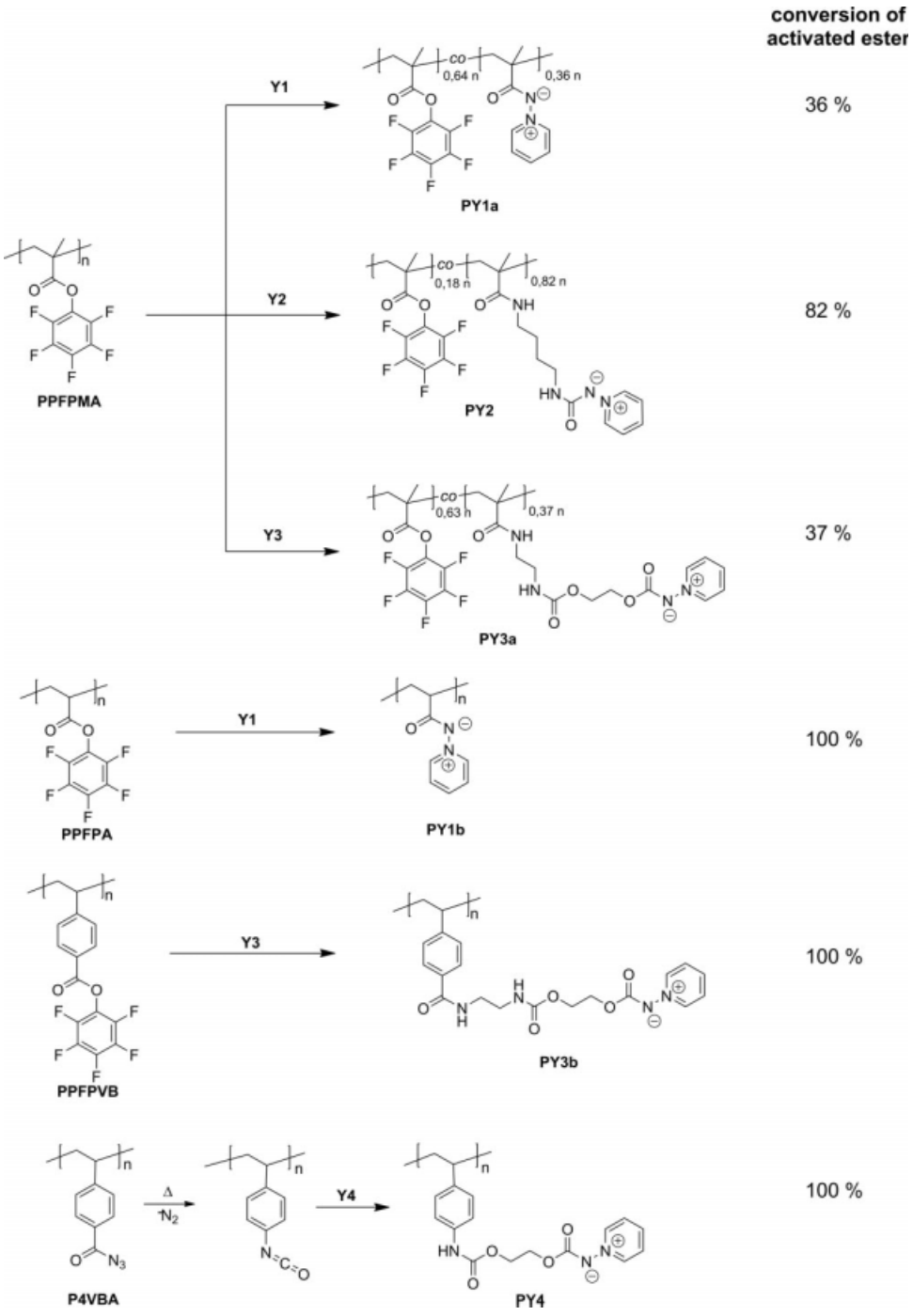
Polymer Analogous Reaction of PPFPA with Y1 (PY1b)

^{1}H NMR (MeOD-d_4): δ = 8.82 (br s, 2H); 8.14 (br s, 1H); 7.78 (br s, 2H); 2.89 (br s, 1H); 2.38–1.60 (br m, 2H).

TABLE 2 Conditions of the Polymerizations of the Activated Ester Monomers

Polymer	Monomer	Solvent	Initiator	T (°C)	t (h)	Precipitated In	Yield (%)
PPFPMA	Pentafluorophenyl methacrylate	THF	AIBN	60	20	Methanol	43
PPFPA	Pentafluorophenyl acrylate	THF	AIBN	60	20	Methanol	80
PPFPVB	Pentafluorophenyl vinylbenzoate	THF	AIBN	60	8	Methanol	76
P4VBA	4-Vinylbenzoyl azide	THF	V-70[a]	32	16	Methanol	48

[a] V-70: 2,2′-Azobis(4-methoxy-2,4-dimethyl valeronitrile).



SCHEME 4 Reactions on reactive precursor polymers to yield the respective photoreactive polymers.

Polymer Analogous Reaction of PPFPVB with Y3 (PY3B)

^{1}H NMR (DMSO-d$_6$): δ = 8.71 (br s, 2H); 8.38 (br s, 2H); 8.01 (br s, 1H); 7.74 (br s, 2H); 7.64–7.22 (br m, 3H); 6.49 (br s, 1H); 4.08 (br s, 4H); 3.15 (br s, 4H); 2.27–0.87 (br s, 3H).

Polymer Analogous Reaction of P4VBA with Y4 (PY4)

^{1}H NMR (DMSO-d$_6$): δ = 9.50 (br s, 1H); 8.72 (br s, 2H); 7.98 (br s, 1H); 7.71 (br s, 2H); 7.18 (br s, 2H); 6.46 (br s, 2H); 4.16 (br s, 4H); 2.23–0.50 (br s, 3H).

Photoisomerization Studies via ^{1}H NMR Spectroscopy

Twenty to thirty milligram of each sample were dissolved in 1 mL of deuterated solvent. The solution was placed in a quartz cuvette and then irradiated for 24 h with 500 W at the wavelengths of 315–390 nm. The reaction mixture was added to an NMR tube, sealed and directly placed in a 300 MHz NMR spectrometer.

Kinetic UV-Vis Measurements

Kinetic measurements were performed by irradiating a solution of each sample for 1 min at 315–390 nm before every measurement.

TABLE 3 Conditions of the Postpolymerization Functionalization of the Polymeric-Activated Esters Yielding Polymeric Ylides

Product	Precursor Polymer	Solvent 1	Functionalized Ylide	Solvent 2 (Total)	T (°C)	t (h)	Precipitated In	Yield (%)
PY1a	PPFPMA	Dioxane	Y1 (1API + NEt_3)	Methanol	25[a]	24	THF	78
	0.79 mmol PFPMA	2.4 mL	0.95 mmol	1.2 mL	50[a]	72		
PY2a	PPFPMA	Dioxane	Y2	Methanol	25[a]	24	Acetone	77
	0.64 mmol PFPMA	2.4 mL	1.00 mmol	3.6	50[a]	72		
PY3a	PPFPMA	$CHCl_3$	Y3	Methanol[b]	50[c]	48	THF	75
	2.98 mmol PFPMA	3.0 mL	3.7 mmol	1 mL	25[c]	120		
PY1b	PPFPA	DMSO	Y1 (1API + NEt_3)	DMSO	25	12	Acetone	78
	0.84 mmol PFPA	1.0 mL	0.91 mmol	1.0 mL				
PY3b	PPFPVB	$CHCl_3$	Y3	$CHCl_3$	25	12	Acetone	74
	0.32 mmol	1.5 mL	0.37 mmol	1.5 mL				
PY4	P4VBA	DMF	Y4	–	70	4[d]	Acetone	34
	1.15 mmol	4 mL	1.39 mmol					

[a] Addition was performed at room temperature (25 °C), after 24 h the reaction temperature was increased to 50 °C.
[b] Triethylamine was added (0.37 mmol).
[c] Addition was performed at 50 °C, after 24 h the reaction temperature was decreased to room temperature (25 °C).
[d] After 4 h unreacted isocyanato groups were quenched by adding 0.5 mL of anhydrous methanol.

RESULTS AND DISCUSSION

Two synthetic routes to obtain polymeric 1-imino pyridinium ylides were investigated. First, three different monomers containing photoreactive 1-imino pyridinium ylide groups were synthesized and successfully polymerized by free radical polymerization. Second, functional molecules containing pyridinium ylide groups were attached to reactive precursor polymers via polymer analogous reactions. For this purpose, three different activated ester polymers, namely poly(pentafluorophenyl methacrylate), poly(pentafluorophenyl acrylate), poly(pentafluorophenyl 4-vinylbenzoate) as well as poly(4-vinylbenzoyl azide) as an isocyanato group generating polymer were synthesized by free radical polymerization. Two different photoreactive amines and one alcohol were synthesized to attach the 1-imino pyridinium ylide groups to the reactive polymers mentioned earlier. The reactions on the polymers were studied with the focus on the conversion of reactive groups. All polymers obtained by both synthetic routes were examined in respect to their photoreaction. Especially, the kinetics of the photoreactions in the polymers were examined by UV-vis spectroscopy and compared to those of their low molecular weight analogues. Thin films of the polymers were fabricated and illuminated. Contact angle measurements were used to reveal differences in wettability.

Synthesis of Monomers M1, M2, and M3

To examine the influence of the substituent on the side of the carbonyl group opposite to the ylide nitrogen atoms on the ratio of diazepine formation versus *N—N* bond cleavage, three different monomers with a systematically varied molecular structure were synthesized (Scheme 2). Hereby, the heteroatoms in the carbamate derivative of M1 and the urea derivative of M3 should favor the diazepine formation upon irradiation, while the aryl substituent in the benzoyl derivative of M2 as a carbon based substituent should influence the photoreaction to yield a significant amount of pyridine elimination.[24,26,28,29] M1[41] was synthesized by carbonyldiimidazole (CDI) activated coupling of hydroxyethyl methacrylate (HEMA), with 1-aminopyridinium iodide (1API) under basic conditions. The ethyl spacer group was introduced to prevent deactivation of the double bond due to conjugation effects with the pyridinium ylide ring. For the synthesis of M2, 4-vinyl benzoic acid was also activated with CDI and allowed to react with the free amine of 1API. The synthesis of M3 started with 4-vinylbenzoyl azide[39] (4VBA), which is known to undergo a Curtius rearrangement at elevated temperatures and thereby rearranges into the corresponding isocyanate. The *in situ* formed isocyanate was then reacted with the free amine of 1API yielding the urethane M3.

All monomers showed an explicit hydrophilic character, which was verified by their solubility in polar solvents, such as methanol, ethanol, DMSO, DMF, NMP and even water for monomer M1. UV-vis spectroscopy showed in each case two characteristic π-π^* absorption peaks corresponding to the pyridinium ylide rings.[42] The absorption maxima of the long wave transition depends on the substituents on the pyridinium ylide carbonyl group due to their electronic influences on the π-π^* transition, which is accompanied by the electron donating character of the ylide nitrogen to the pyridinium ring. Hence, the energy gap can be decreased by substituents with a +M effect and the resulting red shift could be detected in the UV-vis spectra. The absorption maxima were determined to be 330 nm for M1, 353 nm for M2 and 373 nm for M3 in chloroform (see Supporting Information). In addition, a strong negative solvatochromic effect could be observed for all monomers. The bathochromic shifts of the absorption maxima in chloroform relative to methanol confirmed the highly hydrophilic character of the monomers (see Supporting Information).

Polymers PM1, PM2, and PM3

Monomers M1, M2, and M3 were polymerized under free radical polymerization conditions yielding the respective polymers PM1, PM2, and PM3 (see Table 1). Investigations of the purified polymers by ^{1}H NMR spectroscopy showed the characteristic broad peaks in the aromatic region, which could be assigned to the pyridinium ylide ring, confirming that the photoreactive group remained intact during the polymerization. UV-vis measurements confirmed this observation by detecting the same absorption maxima that was found for the respective monomers. Molecular weight characterization was extremely difficult for these mesoionic polymers due to their solubility restriction to polar solvents such as methanol, water, DMSO, NMP, and DMF. GPC measurements of PM1 in water were not successful in determining the molecular weight. Similarly, GPC measurements of PM1, PM2, and PM3 in DMF failed in determining the molecular weight. Also the investigation of the molecular weight by MALDI-TOF was not successful.

The problems of molecular weight determination of PM1, PM2, and PM3 motivated us to break new ground and follow an alternative synthetic route via reactive precursor polymers to yield polymeric pyridinium ylides. In this case the precursor polymer molecular weights could easily be determined by GPC measurements in THF. Reactions on these polymers required, however, specifically functionalized low molecular weight pyridinium ylides (see Scheme 3).

Synthesis of Functionalized 1-Imino Pyridinium Ylides

To investigate the possible tuning of the photoreaction of pyridinium ylides to yield different products, four distinct functionalized ylides have been synthesized. Since the substituent on the side of the carbonyl group opposite to the ylide nitrogen atoms influences the photoreaction pathway, the connection of the spacer group to the ylide moiety was, in analogy to the monomers M1–M3, systematically varied. Y1 as a free amine yields by reaction with a reactive precursor polymer an aliphatic connection of the pyridinium ylide to the polymer backbone and thus should favor the pyridine elimination. In contrast, Y2, Y3, and Y4 as carbamate or urea derivatives should enhance the diazepine formation due to their connection via a hetereoatom.[25,26,28,29] Y1 was formed by deprotonation of 1API with potassium carbonate. The photoreactive alcohol Y4 was synthesized in one step by a ring opening reaction of ethylene carbonate with the free amine of 1API. Y3 as an amino terminated ylide molecule was synthesized by attaching ethylene diamine onto the carboxylated alcohol of Y4. For the preparation of the photoreactive amine Y2, the CDI activated commercially available *N*-BOC-1,4-diaminobutane was reacted with the deprotonated 1API to yield the BOC-protected photoreactive ylide Y2. Deprotection with hydrochloric acid in aqueous media yielded Y2.

^{1}H NMR spectroscopy of the functionalized pyridinium ylides showed in all cases the characteristic multiplets attributed to the pyridinium ring. The UV-vis spectra of Y4, Y2, and Y3 in DMSO clearly showed the long wave absorption band due to the π-π* transition of the aromatic pyridinium cycle (see Supporting Information). As a result of their similar molecular attachment of the spacers to the carboxylic group of the pyridinium ylide, the carbamate derivatives Y4 and Y3 showed the same absorption maxima at 330 nm. In contrast, the urea derivative of Y2 showed a shifted absorption maximum at 358 nm due to the same electronic effects as already discussed for the UV-vis spectra of the monomers M1 and M3 (see Supporting Information). The solubility of the functionalized pyridinium ylides was restricted to polar solvents such as methanol, DMSO, DMF, and NMP. Y3 showed also good solubility in $CHCl_3$ and Y2 was soluble in water.

Reactions on the Precursor Polymers

Polymeric activated esters are well known to react fast and quantitatively with primary and secondary amines in a broad variety of organic solvents.[36] The synthesis and characterization of pentafluorophenyl ester polymers is well established and their reactions with 1-imino pyridinium ylides therefore represent an alternative way to obtain photoreactive polymers with a known molecular weight and polydispersity. However, the restricted solubility of the amino functionalized pyridinium ylides to polar solvents limits the conditions for the reactions on the precursor polymers. In a first attempt poly(pentafluorophenyl methacrylate) (PPFPMA) was reacted with the different amines Y1, Y2 and Y3. The reactions were complicated by differences in solubility of the amines, the precursor polymer and the formed photoreactive polymer. Hence, different solvent mixtures were used to ensure best possible solubility. During the reactions the polymers were kept in solution by changing the composition of the solvent mixture, thereby adjusting its polarity. However, solubility problems still prevented a complete conversion of the active ester groups in PPFPMA. The percentages of attached photoreactive groups could be calculated by integration of the respective ^{1}H NMR spectra and were determined for the reaction of PPFPMA with Y1 to yield PY1a to be in the order of 36%, for the reaction of PPFPMA with Y2 yielding PY2a to be in the order of 82% and in the order of 37% for the reaction of PPFPMA with Y3 yielding PY3a. In other words, in all reactions only copolymer structures were obtained. Nevertheless, UV-vis measurements showed in every case the characteristic long wave π-π* transition band attributed to the pyridinium ylide groups and, therefore, proved the successful coupling to the polymer backbone. The absorption maxima of 300 nm for PY1a, 342 nm for PY2a and 328 nm for PY3a also indicated that the photoreactive moieties were not affected by the coupling reactions.

To overcome the restrained solubility of the PPFPMA polymers during the conversion of activated ester groups, poly (pentafluorophenyl acrylate) (PPFPA) was reacted with Y1 to yield PY1b. In comparison to PPFPMA, which had to be reacted in solvent mixtures, the acrylate-based polymer was soluble in DMSO, which is also a good solvent for the photoreactive amines. Consequently, the reaction with Y1 proceeded quantitatively within 12 h at room temperature in homogeneous solution. Conversion of all activated ester groups was determined by ^{1}H NMR spectroscopy and the even more sensitive method of ^{19}F NMR spectroscopy, which

TABLE 4 Photoreactions of 1-Imino Pyridinium Ylides in Solution

Sample	Solvent	Conversion (%)	Diazepine-Formation (%)	:	Pyridine-Elimination (%)
M1	DMSO	100	100	:	0
PM1	DMSO	100	100	:	0
M2	DMSO	78	100	:	0
PM2	DMSO	100	75	:	25
M3	DMSO	0	0	:	0
PM3	DMSO	0	0	:	0
PY1a	MeOH/dioxane (3:4)	83	17	:	83
PY2a	MeOH/dioxane (1:1)	100	100	:	0
PY3a	MeOH/DMSO (1:7)	100	100	:	0
PY1b	DMSO	100	7	:	93
PY3b	DMSO	100	100	:	0
PY4	DMSO/dioxane (6:1)	100	100	:	0

showed no signals of any remaining pentafluorophenyl groups. In addition, the characteristic bands of the pentafluorophenylester groups at 1781 cm^{-1} and 1515 cm^{-1} in the FTIR spectrum vanished completely. The absorption maximum at 320 nm in the UV-vis spectrum proved the successful attachment of the chromophore to the polymer.

Furthermore, the activated ester polymer poly(pentafluorophenyl 4-vinylbenzoate) (PPFPVB) is known for its highly reactive character toward amines and was, therefore, chosen to examine the influence of higher reactivity combined with better solubility on the conversion of the reactive groups. PPFPVB was reacted with Y3 in chloroform, which is a good solvent for the activated ester prepolymer, the photoreactive amine and the resulting photoreactive polymer PY3b. In this case, the reaction proceeded also quantitatively within 12 h at room temperature. 100% conversion of all activated ester groups was again confirmed by FTIR, ^{19}F NMR, and ^{1}H NMR spectroscopy. Of course, UV-vis spectroscopy showed in analogy to PY3a the same absorption maximum at 328 nm for the carbamate derivative of the pyridinium ylide group of Y3 (see Supporting Information).

An alternative way to the reaction of activated ester prepolymers with amines is the reaction of different alcohols with P4VBA, an isocyanato group generating polymer.[39] For the synthesis of the photoreactive polymer PY4, P4VBA was reacted with Y4 in DMF under anhydrous conditions. At 70 °C isocyanato groups were formed *in situ* by a Curtius rearrangement and reacted directly with the photoreactive alcohol Y4. Once more, FTIR and ^{1}H NMR spectroscopy showed a quantitative conversion of all azide groups. PY4 was obtained as a pure polymer in 35% yield after precipitation in acetone. The low yield can be attributed to the formation of a small percentage of crosslinked material due to traces of water in the reaction mixture, similar to experiments published recently.[39] As expected, because of the same molecular structure as carbamate derivative of the attached pyridinium ylide Y4, PY4 showed the same absorption band as PY3a and PY3b in UV-vis spectroscopy at 328 nm (see Supporting Information).

Photoreaction Studies via ^{1}H NMR Spectroscopy

To examine the performance of the new photoreactive polymers, detailed studies of the photoreaction and especially the ratio of 1,2-diazepine formation versus *N—N* bond cleavage were conducted. This ratio was expected to depend strongly on the molecular structure of the chromophores and should therefore be controllable by the systematic variation of the attachment of the pyridinium ylide group to the spacer groups or the polymer backbone. In addition, the photoreaction of the polymeric pyridinium ylides was compared to their low molecular weight analogues. The isomerization studies were carried out in deuterated solvents in a quartz-cuvette at concentrations of 25 mg/mL. All solutions of polymers and low molecular weight analogues were characterized by ^{1}H NMR spectroscopy, and then irradiated for 24 h at the wavelengths of 315–390 nm. The crude reaction mixture was then characterized again by ^{1}H NMR spectroscopy without any further purification. Overall conversion of the pyridinium ylide chromophores as well as the ratio of formed 1,2-diazepine to the elimination of pyridine by *N—N* bond cleavage were calculated by ^{1}H NMR and are summarized in Table 4.

Even though determination of molecular weight failed for the polymers PM1-PM3, their photoreaction was compared to those of the polymers formed by polymer analogous reactions. Monomer M1 and the respective polymer PM1 showed the quantitative conversion of all pyridinium ylide groups to the 1,2-diazepines upon irradiation in DMSO-d_6, as detected by ^{1}H NMR spectroscopy. In comparison, M2 showed only a 78% conversion of the photoreactive groups to the 1,2-diazepine as only product, whereas PM2 showed a quantitative conversion of the chromophores yielding 25% of pyridine elimination and 75% of the photoisomer. Hereby, the difference to the monomer reaction can be explained by the higher viscosity of the polymer solution in comparison to the viscosity of the monomer solution in the same solvent. The decreased molecular motion leads to fewer intermolecular collisions inhibiting a deactivation of the triplet state and thus favoring the *N—N* bond cleavage.

M3 and PM3 both showed no conversion of the chromophores during irradiation at all. It was assumed that this effect occurs due to the high optical density of the monomer and polymer. Regarding solutions of the same chromophore concentration of M1, M2, and M3 it could be clearly observed that M2 in comparison to M1 already showed an increase of the absorption by the factor 1.5, whereas M3 showed an absorption intensity of even 2.5 times compared to M1. The photochemically formed 1,2-diazepines exhibit an intense π-π^* transition of the nonplanar ring in the range of short wavelengths between 220–250 nm and a prohibited n-π^* transition at 370 nm for M1, 390 nm for M2, and 430 nm for M3. Both transitions overlap with the long wave pyridinium ylide band and therefore reduce the quantum yield of the photoreaction resulting in a deceleration. This effect increases with the optical density of the monomers from M1 over M2 to M3 and could also be observed for the respective polymers PM1, PM2 and PM3.

The photoreactive polymers PY2a, PY3a, PY3b, and PY4, all carbamate or urea derivates, showed quantitative conversion to the respective 1,2-diazepines. No sign of *N—N* bond cleavage could be detected. In comparison, PY1a and PY1b contained pyridinium ylides that were attached by aliphatic groups to the polymer backbone. This different electronic structure strongly influences the photoreaction of these polymers in favor of the excited triplet state and therefore *N—N* bond cleavage.[26,28,29] Irradiation of PY1a for 24 h yielded in a conversion of 83% of all pyridinium ylide groups, whereas in the case of PY1b 100% of the chromophores reacted. The amount of pyridine elimination was significantly higher compared to all other photoreactive polymers. PY1a showed 83% of pyridine formation, while for PY1b even 93% of pyridine formation was observed. In summary, it should be noted that by systematically varying the molecular structure of the pyridinium ylide group on the polymers the ratio of 1,2-diazepine formation to *N—N* bond cleavage can be influenced and diversified from 100% down to 7% of diazepin formation. As a comparison, Figure 1 shows the ^{1}H NMR spectra of PY4 and PY1b before and after 24 h of irradiation.

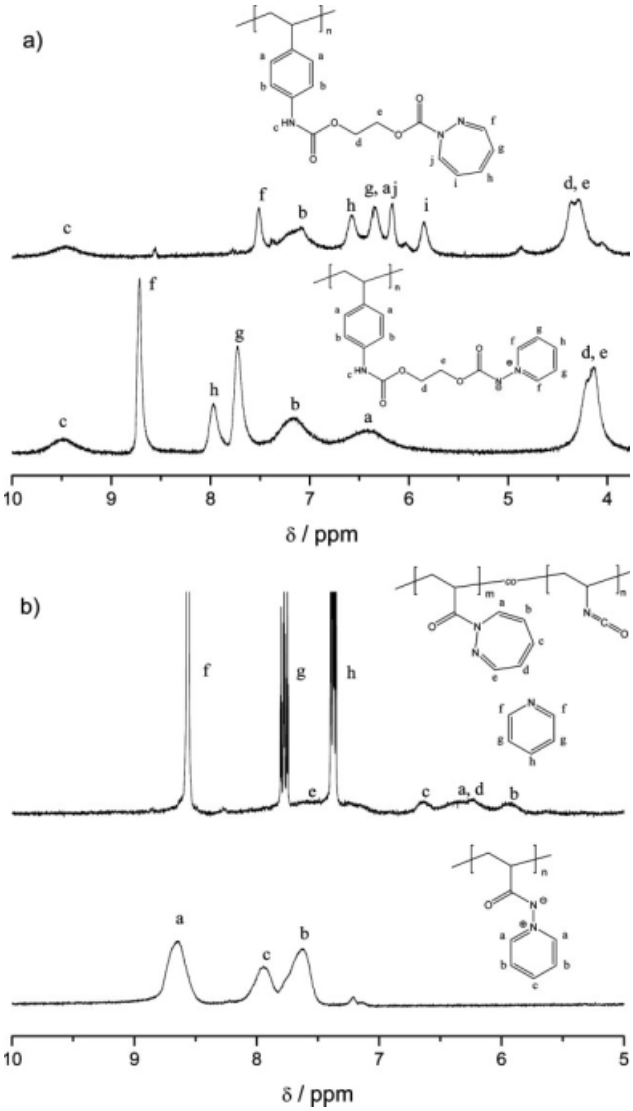


FIGURE 1 ^{1}H NMR spectra in DMSO-d_6 of the photoreactive polymers and their crude photoproducts: (a) PY4 before and after irradiation, (b) PY1b before and after irradiation.

Kinetic UV-Vis Measurements

To confirm and quantify the observed deceleration effect of the photoreaction due to different optical densities of the polymers, kinetic UV-vis measurements in diluted solutions of c = 1.5×10^{-4} mol/L were conducted. The measurements were restricted to the homopolymers PM1, PM2, PY1b, PY3b, and PY4, which consisted of 100% pyridinium ylide repeating units, and their low molecular weight analogues M1, M2, M3, Y3, and Y4. All substances were dissolved in DMSO. Series of UV-vis spectra were recorded, measuring a spectrum each time after every sample was irradiated for 1 min. To prove the stability against further reactions in the dark, a comparative sample of every substance was irradiated for 5 min; a UV-vis spectrum was measured and was then kept in the dark for 1 h before it was measured again. The resulting spectra of all investigated ylides showed no change of the absorption intensity. Time dependent UV-vis spectra were analyzed by the intensity change of the absorption maximum. The absorption maximum at $t = 0$ was set as $[M]_0$ and a plot of $-\ln[M]_0/[M]_t$ versus t resulted in a linear distribution, indicating a first order kinetic in respect to the chromophore concentration as expected. In this case, a linear regression directly yielded the rate constants of the photoreactions. The half-life time for a first-order reaction is defined as $\tau_{[1/2]} = (\ln 2)/k$ and was calculated for every sample. The determined half-life times are listed together with the calculated rate constants in Table 5. Time dependent UV-vis spectra of the photoreaction of PY4 and the -ln$[M]_0/[M]_t$ versus t plots for the calculation of the rate constants for all investigated polymers are shown in Figure 2(a,b), respectively.

All monomers showed a quantitative conversion of the pyridinium ylide groups. In comparison to the results obtained in concentrated solution, this confirms the suggestion that a

TABLE 5 Rate Constants and Half-Life Times for the Photoreactions of Synthesized Photoreactive Polymers and Their Low Molecular Weight Analogues

Polymeric Ylide	k (s^{-1})	$\tau_{1/2}$ (s)	Monomeric Ylide	k (s^{-1})	$\tau_{1/2}$ (s)
PM1	3.68×10^{-3}	188	M1	3.23×10^{-3}	215
PM2	2.56×10^{-3}	271	M2	1.42×10^{-3}	489
PY1b	4.43×10^{-3}	156	–	–	–
–	–	–	M3	0.15×10^{-3}	4,620
PY3b	3.80×10^{-3}	182	Y3	5.10×10^{-3}	136
PY4	2.97×10^{-3}	233	Y4	3.53×10^{-3}	196

higher optical density results in a deceleration of the photochemical rearrangement. The inherent difference of the optical density and its influence on the rate constants of the isomerization process is strongly pronounced for M3. The rate constant is decreased by a factor of 20 compared to M1, while M2 only showed a deceleration factor of 2 compared to M1. Further measurements of the reaction kinetics in more concentrated solutions ($c = 3.0 \times 10^{-4}$ mol/L) confirmed the observation that a higher chromophore concentration increased the optical density and therefore decelerated the photoreaction as well. Comparison of the half-life times for the photoreactions of the carbamate derivatives Y3 and Y4 with those of the monomers M1, M2, and M3, showed that the values were in the same order than those of M1. In case of the polymers PM1, PY3b, and PY4, the rate constant did not vary significantly from those of their low molecular weight analogues, indicating that the reactions in the polymers proceed in the same time scale as those in the monomers. However, for polymer PM2 the photoreaction half-life time decreased compared to M2. The observed effect contradicts the expected deceleration of the isomerization process due to the inhibited molecular motion during the ring expansion in the more viscous polymer solution. It seems that in this case the divergence could be explained by the increased ratio of *N—N* bond cleavage. Although the formed 1,2-diazepines absorbed in the same range of wavelengths, the pyridine elimination led to no deceleration effects as they do not absorb in that region and hence, did not lead to a reduction of the photon density available for the photoreaction. Therefore, PM2 with a ratio of 25% of *N—N* bond cleavage reacted faster than M2 where only the diazepine was detected as photoproduct. In addition the acceleration of the photoreaction in the polymer was also observed by the conversion of the samples for ^{1}H NMR studies mentioned above. After 24 h of irradiation, M2 showed only a conversion of 77% whereas PM2 already reacted quantitatively.

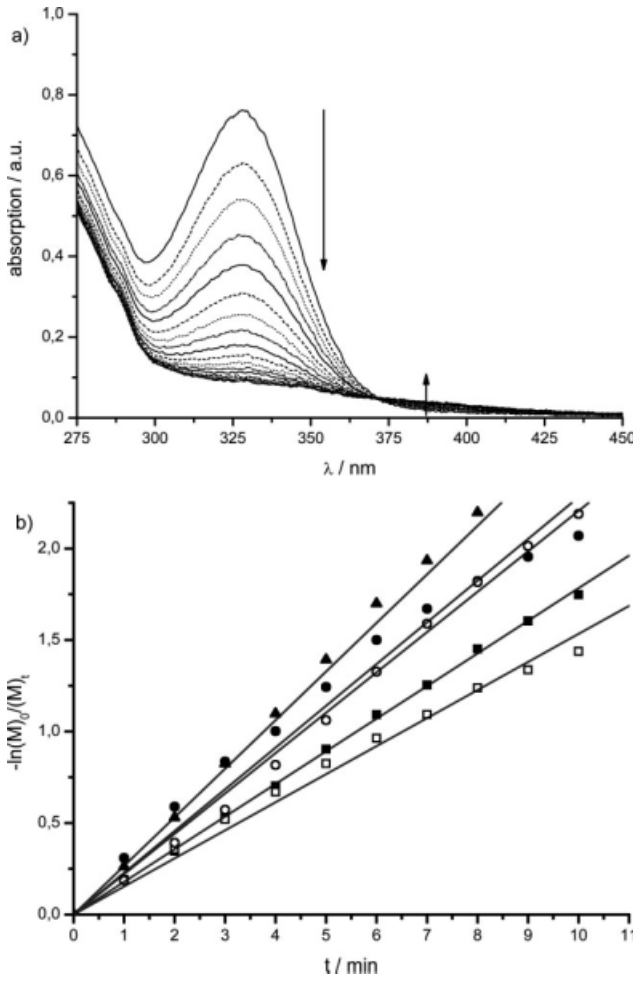


FIGURE 2 (a) Time dependent UV-vis spectra of the photoreaction of PY4 in DMSO, (b) Kinetic plots for the calculation of the rate constants of the photoreaction of PM1 (○), PM2 (□) und PY1b (▲), PY3b (●), PY4 (■).

Photoreactions in Thin Polymer Films

The photoreaction of polymeric pyridinium ylides in a polymer film has already been described in the literature and can be exploited as a negative photoresist.[27] With regard to a possible application of the synthesized polymers for optical data storage or surface modifications, it should be assured that the photoreaction also proceeds quantitatively in thin polymer films. Thin polymer films were prepared by spin coating polymer solutions of PM1, PM2, PY1b, PY3b, and PY4 on glass substrates to investigate the photoreaction, which was monitored by UV-vis spectroscopy in analogy to the experiments of the polymer solutions. The chromophores in all polymer films were transformed to their respective reaction products in quantitative yields after irradiation with UV-light in less than one hour. Figure 3 exemplary shows the UV-vis spectra of the irradiation of a film of PM2. Each

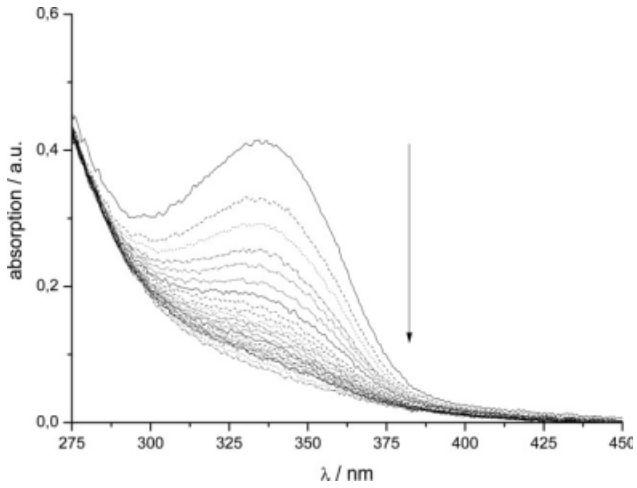


FIGURE 3 UV-vis spectra of the irradiation of a polymer film of PM2.

spectrum was measured after illumination of the sample for 1 min.

Contact Angle Measurements of the Polymer Films

To investigate the change of hydrophilicity of the synthesized polymers, contact angles were measured of the polymer films before and after irradiation. Measurements were performed using the sessile drop method with 40 individual measurements being average. The contact angles measured before and after irradiation are listed in Table 6.

For the polymers PM1 and PY1b as water-soluble polymers no contact angles were determined before irradiation. After irradiation, all films showed increased contact angles of 70 $\pm$ 5°, thus signifying a drastic change in wettability. Noteworthy, irradiation of PY1b resulted in a highly crosslinked material due to the dominating pyridine elimination, which results in the formation of reactive nitrene and isocyanato groups. For the non water-soluble polymers PM2 and PY4 contact angles increased by 56° and 37°, respectively.

CONCLUSIONS

In summary, we have described the synthesis of polymeric 1-imino pyridnium ylides via two synthetic routes, being either the polymerization of 1-imino pyridinium ylide containing monomers or the attachment of 1-imino pyridinium ylides onto reactive precursor polymers. Three different 1-imino pyridinium ylides containing monomers could successfully be polymerized under free radical polymerization conditions, however, resulting in problems with the determination of the molecular weight. Thus, three different 1-imino pyridinium ylides were efficiently and quantitatively attached to different reactive precursor polymers, such as poly(pentafluorophenyl acrylate), poly(pentafluorophenyl 4-vinylbenzoate) and poly(4-vinylbenzoyl azide). Depending on the substituents of the 1-imino pyridinium ylides, the photoreaction could be controlled to be either a quantitative photoisomerization to the 1,2-diazepine containing polymers or a photoelimination of 93% of pyridine. The half-life times for the photoreactions of the synthesized photoreactive polymers and their low molecular weight analogues were found to be very similar for all cases. Investigations of the photoreactions of thin polymer films of the synthesized ylide containing polymers showed a dramatic increase of contact angles of water on those films after irradiation.

TABLE 6 Contact Angles of Thin Polymer Films Before and After Irradiation

Polymer	θ (Nonirradiated) (°)	θ (Irradiated) (°)
PM1	–[a]	70.2
PM2	19.1	75.2
PY1b	–[a]	67.5
PY4	36.3	73.3

[a] Soluble in water.

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