

# Polysilylenes with ethynylphenyl substituents

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Ethynylphenyl-methyldichlorosilane (EPDMS) has been prepared as a new monomer for the synthesis of polysilylenes with triple bonds attached to the catenated Si chain. A series of copolymers with methylphenyldichlorosilane (MPDS) as well as the homopolymer, PEPMS, have been synthesized. The content of ethynylphenyl substituents was quantitatively analyzed by FTIR spectroscopy. The optical properties of the new polymers were studied with respect to potential  $\pi$ - $\sigma$  interaction. No significant bathochromic shift of the UV-absorption maximum could be detected. Unexpectedly, increasing content of incorporated EPMS units led to a decrease of the ( $\sigma$ - $\sigma^*$ ) absorption. The ethynylphenyl-substituted polysilylenes exhibited strong, temperature-dependent fluorescence in solution as well as in films.

## 1. Introduction

Due to the delocalization of  $\sigma$ -orbitals of the catenated silicon chain, catena-Si structures are comparable to conjugated  $\pi$ -systems [1, 2]. The  $\sigma$ -orbital delocalization depends strongly on the geometry of the chain segments, i.e. bonding angles between Si atoms [3, 4]. However, electronic interaction with adjacent  $\pi$ -conjugated moieties [5, 6] also plays a crucial role, e.g. poly(methylphenylsilylene) absorbs light at 345 nm, whereas poly(cyclohexylmethylsilylene) displays an absorption maximum at 316 nm. Studies on geometrically confined oligomeric silanes, such as cyclophanes bridged by oligosilanes, have shown that  $\pi$ - $\sigma$  interaction can result in extended delocalization [7, 8], manifest in pronounced bathochromic UV-shifts.

Interaction of  $\sigma$ - and  $\pi$ -delocalized systems has been the subject of several recent studies [9-12], motivated by the interesting  $\chi^{(3)}$  nonlinear optical (NLO) properties of polysilylenes [13, 14] as well as the electroluminescence observed in such systems [15]. High  $\chi^{(3)}$  values of the order of  $10^{-9}$  esu have been measured for a material obtained from the polymerization of diethynyldiphenylsilane, which results in a combination of oligosilylene and carbosilylene segments [16, 17]. Therefore it appears intriguing to study the influence of adjacent acetylenic moieties on the optical properties of polysilylenes.

In this paper the synthesis of polysilylenes substituted with ethynylphenyl substituents is described, i.e. polysilylenes with triple bonds adjacent to the main chain. A first description of the UV-absorption behavior of this class of polymers is given.

## 2. Experimental

### Synthesis

#### *Synthesis of ethynylphenyl-methyldichlorosilane*

All manipulations were carried out under Ar. In a 500 mL three-neck flask, equipped with an addition funnel and magnetic stirrer, 170 ml *n*-BuLi solution (1.45 M, obtained from Aldrich) was dissolved in 150 mL diethyl ether under cooling ( $-18$  °C). Subsequently, 19.2 mL (0.175 mol) of

phenylacetylene was added dropwise. The phenylacetylid prepared in this manner was then slowly added to 300 mL (2.6 mol, large excess) methyltrichlorosilane dissolved in 900 mL diethyl ether under stirring. The addition funnel employed was kept at  $-18$  °C. After addition of the lithium-phenylacetylid, the suspension was stirred for another 30 min. Subsequently, Li salts were removed by filtration, and the diethyl ether and excess methyltrichlorosilane distilled off. The product was distilled repeatedly and finally obtained as a clear liquid (65 °C; 6 mm Hg). Purity according to GC: > 97%; final yield 45%.

<sup>1</sup>H NMR: (CDCl<sub>3</sub>,  $\delta_{TMS}$  in ppm): 0.81 (s, -CH<sub>3</sub>, 3 protons); 7.16 (t, -CH para-pos., 1 proton); 7.24 (t, -CH meta-pos., 2 protons); 7.29 (d, -CH ortho-pos., 2 protons); <sup>13</sup>C{<sup>1</sup>H}-NMR: (CDCl<sub>3</sub>,  $\delta_{TMS}$  in ppm): 7.46 (-CH<sub>3</sub>); 86.92 (C<sub>1</sub>, ac.); 107.88 (C<sub>2</sub>, ac.); 120.65 (C<sub>3</sub>, ar ipso); 128.46 (C<sub>4</sub>, ar meta); 130.23 (C<sub>5</sub>, ar para); 132.46 (C<sub>6</sub>, ar ortho)

#### *Copolymerization of methyl-phenyldichlorosilane and ethynylphenyl-methyldichlorosilane*

The procedure described here for the copolymer 51/49 P(MPS/EPMS) is representative for the synthesis of all copolymers. Methylphenyldichlorosilane (MPS) was obtained from Petrarch (ABCR). The two monomers were added in a stepwise manner in this case. 11.5 mL toluene was added to a 50 mL flask equipped with a reflux condenser and a magnetic stirring bar. A Na dispersion (0.55 g Na; 24 mmol) was prepared under strong stirring and refluxing of toluene. Subsequently 1.07 g (6 mmol) of methylphenyldichlorosilane was added to the Na dispersion. During the subsequent exothermic reaction the reaction mixture turned blue. After 10 min reaction time, 1.2 g (6 mmol) of the ethynylphenyl-methyldichlorosilane was added, which led to a brown color during the next 30 min. After 4h total reaction time the polymerization was terminated and simultaneously the polymer precipitated by the addition of an excess of methanol (40 mL). The residue was redissolved in toluene and then filtered to remove NaCl and insoluble product fractions, which were analyzed separately. The soluble copolymer was reprecipitated with methanol and dried at 75 °C. 245 mg (17%) of a yellow powder were obtained. Molecular weights are given in Table 1.

<sup>1</sup>H and <sup>13</sup>C-NMR spectra were recorded on a Bruker AC 250 spectrometer, at 250 and 56.3 MHz, respectively. UV spectroscopy was performed on a Philips PU 8720 UV/vis

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scanning spectrometer. UV spectra were measured in cyclohexane. Fluorescence spectra were obtained on a SLM Instruments SPF-500 C spectrometer, with excitation wavelengths of 280 nm and 345 nm. The measurements were carried out at ambient temperature.

FTIR spectra were recorded on a Biorad FTS-60 spectrometer. Thin films were prepared by casting toluene solutions on KBr discs. Spectra were recorded in the absorbance mode for quantitative comparison.

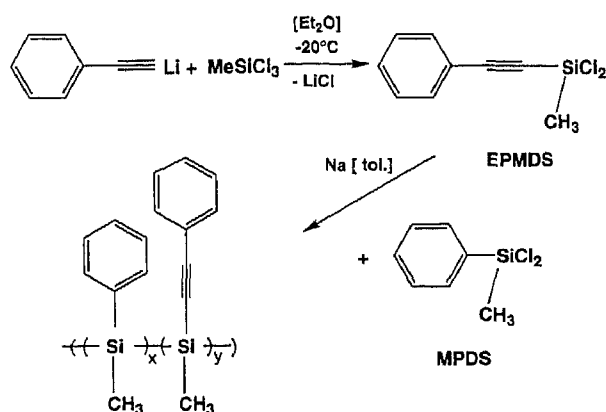
GPC measurements were performed with a set of  $\mu$ -Styragel columns ( $10^5 + 10^4 + 10^3 + 500 \text{ \AA}$ ) guard column. Molecular weights are referenced to narrow polystyrene standards.

### 3. Results and discussion

#### 3.1. Synthesis and structural characterization

The synthetic route employed for the monomer synthesis and polymerization is shown in Scheme 1. Ethynylphenyl-methyldichlorosilane (EPMS) was obtained by reaction of ethynylphenyllithium with methyltrichlorosilane. A large excess of methyltrichlorosilane (15–20 fold) had to be used in order to avoid formation of di- and trisubstituted products. Apparently, the ethynylphenyl group facilitates further substitution reactions. Repeated distillation yielded the EPMS monomer (purity > 97% (GC)) in an overall yield of 45%. In the ensuing discussion, the ethynylphenyl-methylsilylene unit will be designated EPMS, and the methylphenylsilylene unit will be abbreviated MPS. The corresponding dichlorosilane monomers will be termed EPMS and MPDS, respectively.

When comparing the copolymerization of EPMS and MPDS with the homopolymerization of MPDS, pronounced differences were observed: (i) EPMS showed higher reactivity than MPDS. Addition of this monomer to the Na dispersion in the Wurtz-type coupling reaction always caused a strongly exothermic reaction. (ii) When both monomers were added simultaneously, only cyclic and low molecular weight oligomeric products were obtained; (iii) raising the fraction of EPMS-monomer in the monomer feed led to an increasing amount of insoluble, crosslinked products.



Whereas PMPS is a white polymer, the products of the copolymerization were obtained as yellow, powdery materials. The intensity of the yellow color depended on the fraction of EPMS-units built in.

In order to increase the yield of linear high polymer, the reaction was carried out in a stepwise manner. The polymerization was started by addition of MPDS to the refluxing Na dispersion. After 10 min, the EPMS-monomer was added. This always resulted in an exothermic reaction. Unfortunately the desired linear polysilylenes were always obtained in low yields due to the formation of cyclic silanes and crosslinked material. Table 1 gives an overview of the copolymers prepared in this manner.

Table 1. Monomer feed composition for copolymers with EPMS units prepared.

Monomer feed	Yield	$M_n$	$M_w$	$M_w/M_n$
90/10 P(PMS/EPMS)	7.0%	2400	12 700	5.00
80/20 P(PMS/EPMS)	9.3%	3 200	26 400	8.25
62/38 P(PMS/EPMS)	3.5%	6 200	11 900	1.92
40/60 P(PMS/EPMS)		not determined		
10/90 P(PMS/EPMS)	6.5%	5 000	26 400	8.25
PEPMS I	7.8%	3 800	7 800	2.60
PEPMS II	8.5%	40 900	71 800	1.75
51/49 P(PMS/EPMS) <sup>a</sup>	17 %	1 029 000	2 297 000	2.23

<sup>a</sup> This copolymer was prepared from a different monomer batch.

The copolymers were characterized by <sup>1</sup>H and <sup>13</sup>C solution NMR spectroscopy. Figure 1 shows the <sup>13</sup>C-NMR spectrum of PEPMS. The resonances of the acetylenic carbons were strongly broadened and of low intensity. Similar observations are known from other polymers with acetylenic units [17] and can partly be ascribed to the presence of different monomer sequences in the copolymers (i.e. different environments of the acetylenic side chains) and partly to the unfavorable NMR-relaxation of substituted acetylene groups (long  $T_1$ -times).

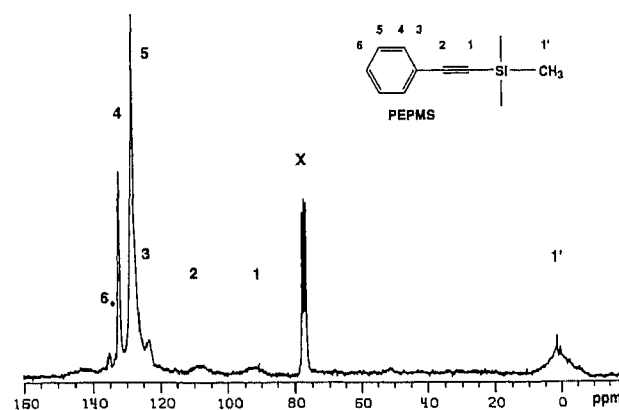


Fig. 1. <sup>13</sup>C-NMR spectrum of the soluble fraction of PEPMS (X: CDCl<sub>3</sub>).

Analysis of the copolymer composition by <sup>13</sup>C-NMR was impossible due to the badly resolved signals of the acetylenic carbons and the overlap of other resonances. In order to verify the incorporation of ethynyl-phenyl units in the soluble product fraction, FTIR spectra were employed to analyze the content of acetylenic units in the soluble fraction of the polymers.

Figure 2 shows a comparison of the FTIR spectra of the copolymers P(MPS/EPMS) and the homopolymer, PEPMS. All spectra are normalized to the intensity of the band series of the aromatic units at 1800–2000  $\text{cm}^{-1}$  and 3000–3100  $\text{cm}^{-1}$ . The growing intensity of the band at

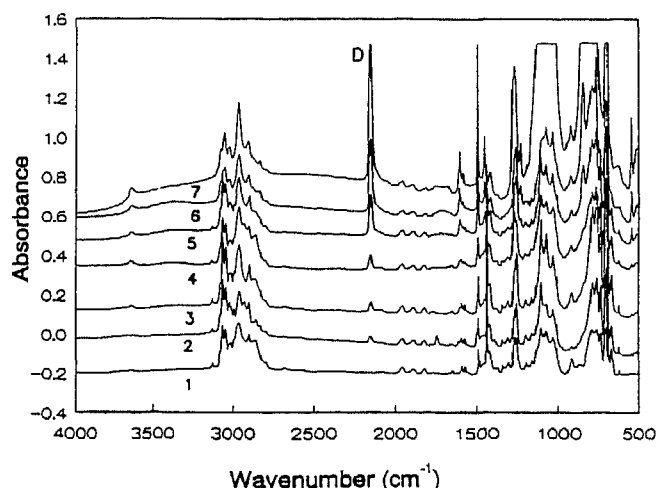


Fig. 2. FTIR spectra of the soluble copolymer fractions recorded in absorption mode. C≡C stretching vibration ( $2160\text{ cm}^{-1}$ ) is marked with D. From bottom to top: increasing content of phenylethynyl units; numbers correspond to the polymer compositions given in Table 2.

$2150\text{ cm}^{-1}$  (C≡C stretching vibration) evidences clearly the incorporation of the acetylenic side chains into the soluble product fraction of the copolymerization. Furthermore, the fraction of ethynylphenyl side chains built in is dependent on the composition of the monomer feed.

When the integral band intensity of the  $2160\text{ cm}^{-1}$  band for the PEPMS homopolymer is assumed to represent 100% ethynylphenyl-substitution, the composition of the copolymers can be calculated (Table 2).

Table 2. Fraction of acetylenic units in copolymers.

Polymer	Mon. feed	In Fig. 2	C≡C content (%)
PPMS	0/100	1	0
P(MPS/EPMS)	90/ 10	2	3.7
P(MPS/EPMS)	80/ 20	3	6.7
P(MPS/EPMS)	62/ 38	4	11.1
P(MPS/EPMS)	40/ 60	5	35.6
P(MPS/EPMS)	11/ 89	6	65.2
P(MPS/EPMS)	100/ 0	7	100

Clearly, the percentage of ethynylphenyl side chains in all cases is lower than the fraction of EPMS employed in the monomer feed. This may either be due to preferential incorporation of EPMS in cyclic products or to facilitated crosslinking induced by the acetylenic side chain. In the latter case, one should expect a large fraction of ethynylphenyl side chains in the insoluble product fraction. The dependence of the copolymer composition on the monomer feed is depicted graphically in Fig. 3.

FTIR spectra of the insoluble side-product fraction have also been recorded in order to confirm the results of Fig. 3. The spectra resembled strongly the spectra obtained for the soluble product fraction. In some cases, the band at  $2160\text{ cm}^{-1}$  exhibited a strongly nonsymmetrical shape, which led us to the tentative conclusion that the insoluble product fraction is due to crosslinking reactions that occur in the vicinity of the ethynyl moiety. If this is the case, the soluble polymer fraction is likely to be branched.

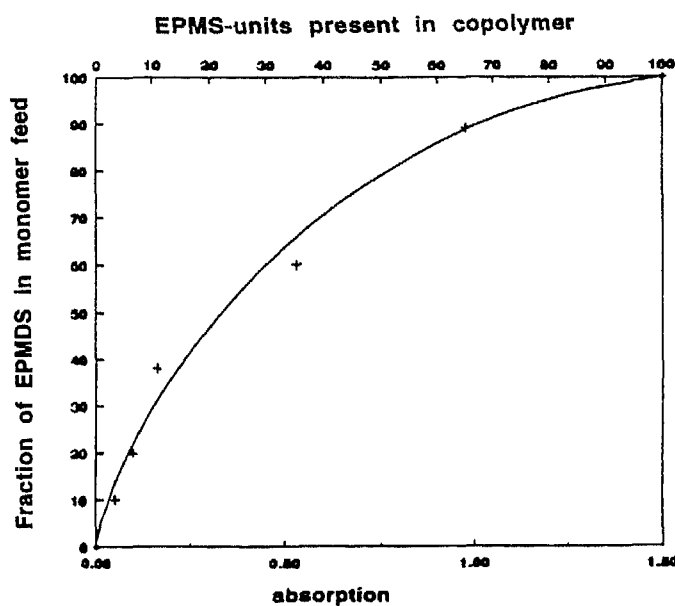


Fig. 3. Fraction of built-in phenylethynyl units (PEMS) as determined by quantitative FTIR analysis vs. the percentage of corresponding dichlorosilane in the respective monomer feed.

### 3.2. Absorption properties

For the new copolymers, peculiar variations of the backbone absorption maximum had been expected due to interaction of the  $\sigma$ - and  $\pi$ -conjugated, delocalized system. PMPS displays two absorption bands in the UV. The lowest energy transition ( $\sigma$ - $\sigma^*$ ) is found at approximately 340 nm ( $\epsilon=9000$ ). The second transition is observed at 280 nm and typical for polysilylenes with  $\pi$ -conjugated substituents directly attached to the backbone. This transition has been explained as a  $\pi$ - $\pi^*$  transition, occurring in the individual phenyl side chains. However, in contrast to our expectations, UV spectra showed no bathochromic shift as may be expected in the case of extension of the delocalized system. Figure 4 shows a comparison of the UV spectra of PMPS and 51/49 P(MPS/EPMS).

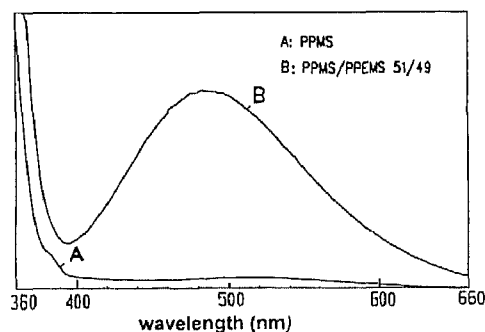


Fig. 4. Comparison of the UV spectra of PMPS and the copolymer 51/49 P(MPS/EPMS).

The unexpected decrease of the ( $\sigma$ - $\sigma^*$ ) transition is an effect observed for all copolymers with increasing fraction of EPMS units. PEPMS shows only an absorption band centered at 280 nm; the  $\sigma$ - $\sigma^*$  transition is lost. Figure 5 shows the decrease of the intensity of the backbone related

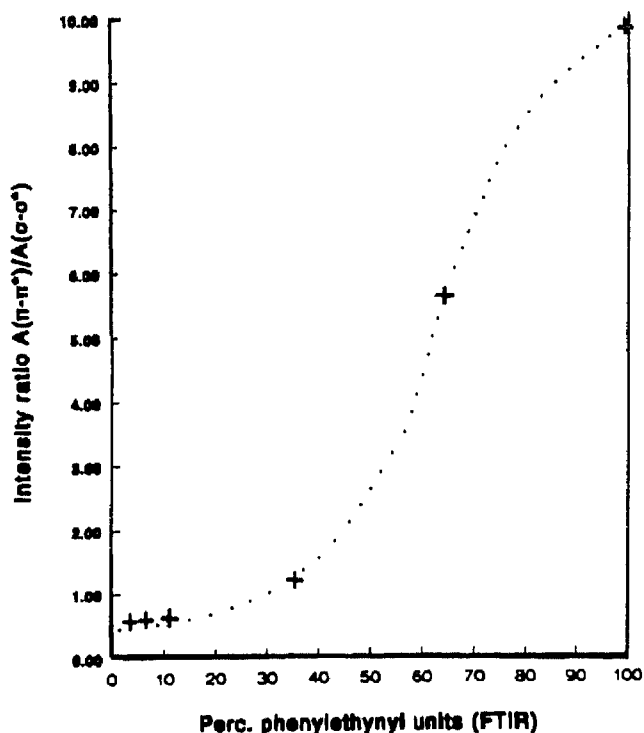


Fig. 5. Ratio  $A(\pi-\pi^*)/A(\sigma-\sigma^*)$  vs. composition of the copolymers.

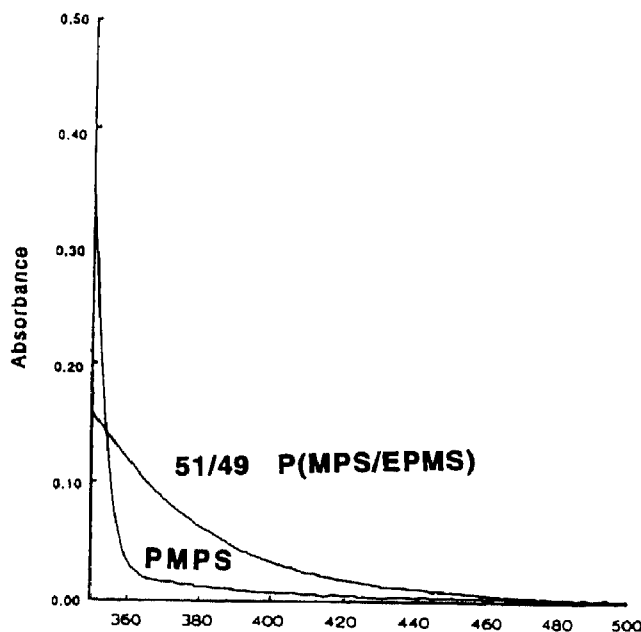


Fig. 6. Long-wavelength part of the UV absorption of PMPS and 51/49 P(MPS/EPMS).

transition relative to the  $(\pi-\pi^*)$  transition of the phenyl side chains. Apparently copolymerization of EPMS units causes a decrease of  $\sigma$ -conjugation.

A comparison of the long-wavelength part of the UV spectra of PMPS and the copolymers (Fig. 6) reveals that for the copolymers the spectrum "trails" into the visible. This may explain the yellow and in some cases orange color of the P(MPS/EPMS) copolymers. A similar effect has been reported recently by Kminek et al. [18] for polysilanes substituted with other chromophoric groups.

In contrast to PMPS, the new copolymers showed intense, very broad fluorescence bands centered at 480 nm. This is illustrated by the comparison of the fluorescence spectra of PMPS and PEPMS in Fig. 7. The sharp, intense emission from the  $\sigma-\sigma^*$  state on the left side of the spectra, which is common for polysilanes, was not recorded and will therefore not be discussed. Excitation wavelengths of 280 nm and 345 nm,  $\lambda_{\text{max}}$  of the  $\pi-\pi^*$  and the  $\sigma-\sigma^*$  transitions, respectively, were chosen to generate the excited states. The fluorescence spectra shown in Fig. 7 were recorded upon excitation at 345 nm. Excitation at 280 nm did not result in fluorescence. The intensity of the fluorescence grows with increasing fraction of built in EPMS groups. Generally, the emission behavior resembles the fluorescence of naphthyl-substituted polysilylene copolymers [19]. In that case it was concluded that the formation of intramolecular excimers between two adjacent naphthalene groups caused the broad emission. Similar excimer formation may also be responsible for the fluorescence observed in our case. This is supported by the fluorescence spectra of thin, spincoated films, which showed fluorescence at 410 nm upon excitation at 345 nm. Excimer formation in the solid may be prevented by low mobility below  $T_g$ . Further optical measurements are necessary to shed light on the optical properties of the copolymers.

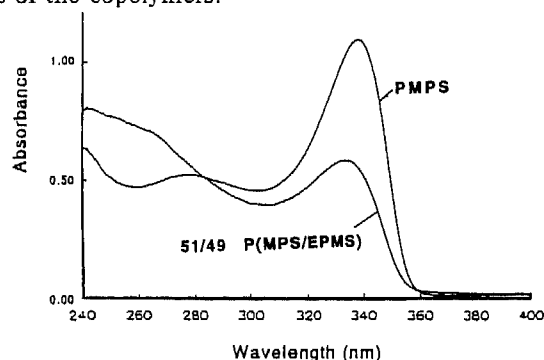


Fig. 7. Comparison of fluorescence spectra of PMPS and 51/49 P(MPS/EPMS) copolymer (excitation at 345 nm).

#### 4. Conclusions

EPMS has been synthesized and copolymerized to prepare polysilylene copolymers and the respective homopolymer with triple bonds adjacent to the main chain. Quantitative FTIR spectroscopy was employed to determine the composition of the materials. Generally, the percentage of EPMS units incorporated into the soluble polymer fraction was lower than the percentage used in the monomer feed.

Unexpectedly, the absorption properties of the new copolymers showed no strong deviation from the spectrum of PMPS. However, increasing the fraction of EPMS units led to gradual disappearance of the backbone related  $(\sigma-\sigma^*)$  absorption. Strong fluorescence bands were observed for the new copolymers, which were centered around 480 nm.

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