Polymer 123 (2017) 81-86

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Thermodynamically stable, highly emissive poly(diphenylacetylene) derivative containing long alkyl side chain without silylene linkage

Young-Jae Jin^a, Yuto Kawamura^b, Masahiro Teraguchi^{b,*}, Toshiki Aoki^{b,**}, Giseop Kwak^{a,***}

^a Department of Polymer Science & Engineering, Polymeric Nanomaterials Laboratory, School of Applied Chemical Engineering, Kyungpook National University, 1370 Sankyuk-dong, Buk-ku, Daegu 702–701, South Korea

^b Department of Chemistry and Chemical Engineering, Graduate School of Science and Technology, Center for Transdisciplinary Research, Niigata University,

Ikarashi 2-8050, Nishi-ku, Niigata 950-2181, Japan

ARTICLE INFO

Article history: Received 16 May 2017 Received in revised form 27 June 2017 Accepted 4 July 2017 Available online 5 July 2017

Keywords: Poly(diphenylacetylene) Photoluminescence Thermodynamic stability

ABSTRACT

A PDPA derivative with a long alkyl side chain connected directly onto the backbone (1) was synthesized and compared to a corresponding polymer with a silylene linkage between the side chain and the backbone (2). Polymers 1 and 2 showed similar solubilities: both polymers dissolved well in organic solvents such as toluene, THF, and chloroform but not in polar solvents such as DMF and alcohols. When cast from toluene solutions, smooth and transparent films were readily obtained. Thermogravimetric analysis showed that 1 was more thermally stable than 2 owing to the absence of the relatively weak silylene linkage. Differential scanning calorimetry showed that 1 exhibited a local thermodynamic relaxation due to the long alkyl side chains at a higher temperature than 2. In photoluminescence spectroscopy, 1 was found to be more emissive, with quantum yields being as high as 63.1 and 27.4% in solution and films, respectively, while those of 2 were 49.4 and 20.6%. Consequently, 1 was more thermally stable, stiffer, and more emissive than 2.

© 2017 Elsevier Ltd. All rights reserved.

1. Introduction

Conjugated polymers (CPs) are key materials for optoelectronic device applications. Among them, poly(diphenylacetylene)s (PDPAs) and related nano-sized and hybrid materials have recently attracted great interest as optical sensors, imaging probes, and actuators in addition to their applications as gas-permeable membranes [1]. In general, conventional CPs show remarkably attenuated photoluminescence (PL) due to the intense intermolecular π - π interactions and dense chain packing structures caused by their intrinsically planar geometries. On the other hand, PDPAs show considerable emission even in the solid state because of their non-planar geometries and highly twisted backbones [1]. The PL of PDPAs is known to originate from an intramolecular excimer formed in the intramolecular stack structure (IaSS) of the pendant

phenyl rings [2]. As is common with CPs, alkyl side chains have been attached to these pendant phenyl rings to disrupt molecular symmetry, leading to improved solubility in common organic solvents. On the other hand, very unique PL emission behavior not usually expected in CPs is seen in PDPAs. As the chain conformation differs considerably depending on the length and/or the substitution position of the alkyl side chains, changing these factors can have a significant effect on the resulting PL emission. For example, long alkyl chains serve as an internal plasticizer to loosen the IaSS, leading to significantly enhanced PL emission [2–4]. In particular, when alkyl chains are attached to the para positions of the side phenyl rings, PDPAs become more emissive through a highly efficient radiative emission decay channel [5]. Therefore, the alkyl side chains play a crucial role in maximizing the PL emission when designing novel PDPA derivatives for advanced applications. However, there is one factor that has been overlooked in previous synthetic strategies: the use of silylene linkages between the alkyl side chains and the backbone. Early on, Masuda et al. synthesized PDPA derivatives containing silylene linkages by attaching the alkyl chains to one of the two phenyl rings through a substitution reaction between lithiated phenyl groups and trialkylchlorosilanes







^{*} Corresponding author.

^{**} Corresponding author.

^{***} Corresponding author.

E-mail addresses: teraguti@eng.niigata-u.ac.jp (M. Teraguchi), toshaoki@eng. niigata-u.ac.jp (T. Aoki), gkwak@knu.ac.kr (G. Kwak).

during the synthesis of the corresponding monomers [6]. Since then, silylene linkages have become a staple for the synthesis of PDPA derivatives. Despite the fact that silicon has a larger atomic radius and adopts higher coordination numbers than carbon, the influences of the silylene linkage on the thermal stability, thermodynamic, and PL properties of PDPAs have never been examined in detail. Although a new category of PDPA derivatives has recently been synthesized with polymethylated ring moieties fused to the pendant phenyl rings, their physical properties other than their gas permeabilities were not examined [7]. In this study, we synthesized a new PDPA derivative having a long alkyl side chain without a silylene linkage (**1** in Fig. 1) and compared its properties with those of an analogous polymer containing a silylene linkage (**2** in Fig. 1). Herein, we describe the details of the resulting thermogravimetric, thermodynamic, and spectroscopic analyses.

2. Experimental section

2.1. Materials

Polymer **2** was synthesized according to a method reported in the literature [8]. The monomer of **1** (**5** in Scheme 1) was synthesized with reference to literature methods [9,10]. $Pd(PPh_3)_2Cl_2$ was prepared by mixing stoichiometric amounts of $PdCl_2$ and triphenylphosphine in hot DMF. $Pd(dppf)Cl_2$ and other reagents were purchased from TCI Co. and used without further purification. Dehydrated solvents (THF and diethyl ether) were obtained from Kanto Chemical Co. Other chemicals including solvents were purchased from Aldrich and TCI and used as received.

2.2. Synthesis of 1 (Scheme 1)

2.2.1. 1-Bromo-4-octadecylbenzene (3)

A three-necked flask was equipped with a Dimroth condenser, dropping funnel, magnetic stirrer bar, and a three-way stopcock then flushed with dry nitrogen. Magnesium turnings (0.63 g, 25.9 mmol), a catalytic amount of iodine, and dry THF (2 mL) were placed in the flask. The mixture was then stirred until the brown color of the iodine disappeared. 1-Bromooctadecane (8.63 g, 25.9 mmol) in dry THF (15 mL) was added dropwise at a rate sufficient to cause gentle self-refluxing. When the addition was finished, the reaction mixture was stirred for an additional 30 min at 40 °C. Another three-necked flask was equipped with a Dimroth condenser, magnetic stirrer bar, rubber septum, and threeway stopcock and flushed with dry nitrogen. 1,4-Dibromobenzene (6.11 g, 25.9 mmol), Pd(dppf)Cl₂ (212 mg, 0.259 mmol), and dry diethyl ether (15 mL) were placed in the flask and the solution was warmed to 40 °C. The above-synthesized 1-octadecylmagnesium bromide was then slowly added through a $\text{Teflon}^{\circledast}$ cannula at 40 °C with stirring. The resulting mixture was refluxed for 2 days and then poured into water. After removal of the catalyst residue by filtration, the filtrate was extracted with diethyl ether. The organic layer was washed with brine and dried over anhydrous MgSO₄, and the solvent was evaporated. The resulting crude product was purified by flash silica gel column chromatography (eluent: hexane) to give **3** (5.27 g, 50%) as a white solid. ¹H NMR (400 MHz, CDCl₃) δ 7.38 (d, J = 8.36 Hz, 2H), 7.05 (d, J = 8.36, Hz, 2H), 2.55 (t,



Fig. 1. Chemical structures of PDPAs without (1) and with (2) a silylene linkage.

J = 7.53 Hz, 2H), 1.57 (m, 2H), 1.34–1.19 (m, 31H), 0.88 (t, *J* = 6.65 Hz, 3H).

2.2.2. 2-Methyl-4-(4-octadecylphenyl)-3-butyn-2-ol (4)

3 (2.00 g, 4.88 mmol), triphenylphosphine (257 mg, 0.98 mmol), copper(I) iodide (278 mg, 1.46 mmol), Pd(PPh₃)₂Cl₂ (175 mg, 0.25 mmol), and triethylamine (20 mL) were placed into a threenecked flask equipped with a Dimroth condenser, three-way stopcock, magnetic stirrer bar, and rubber septum. 2-Methyl-3butyn-2-ol (431 mg, 5.12 mmol) was then added to the solution. The resulting mixture was refluxed and stirred for 24 h. After removal of the solvent by evaporation, the crude residue was extracted with diethyl ether, and the ether solution was washed with 2 N HCl aq., sat. NaHCO₃ aq., and brine and dried over anhydrous MgSO₄. The solvent was evaporated and the obtained crude product was purified by flash silica gel column chromatography (eluent: hexane:ethyl acetate 4:1 v/v) to give 4 (704 mg, 35%) as a white solid. ¹H NMR (400 MHz, CDCl₃) δ 7.32 (d, J = 8.32 Hz, 2H), 7.11 (d, J = 8.32 Hz, 2H), 2.58 (t, J = 7.53 Hz, 2H), 2.00 (s, 1H, -OH), 1.61 (s, 6H), 1.60-1.56 (m, 2H), 1.34-1.19 (m, 31H), 0.88 (t, 3H, I = 6.64 Hz).

2.2.3. 1-(4-Octadecylphenyl)-2-phenylacetylene (5)

A heterogeneous solution of 4 (660 mg, 1.60 mmol), bromobenzene (251 mg, 1.60 mmol), Pd(PPh₃)₂Cl₂ (112 mg, 0.16 mmol), copper(I) iodide (30 mg, 0.16 mmol), and tetrabutylammonium iodide (59 mg, 0.16 mmol) in a mixture of toluene (1 mL) and 5 M NaOH aq. (2.5 mL) was degassed by sonication under reduced pressure for a short time. The mixture was heated at 80 °C for 24 h. and then cooled to ambient temperature. The reaction solution was filtered through a silica gel pad, and the filtrate was concentrated using a rotary evaporator. The crude product was purified by flash silica gel column chromatography (eluent: hexane) to give the desired product (290 mg, 42%) as a white solid. ¹H NMR (400 MHz, $CDCl_3$) δ 7.56–7.49 (m, 2H), 7.44 (d, J = 8.24 Hz, 2H), 7.38–7.28 (m, 3H), 7.16 (d, J = 8.24 Hz, 2H), 2.61 (t, J = 7.53 Hz, 2H), 1.61 (m, 2H), 1.35-1.20 (m, 31H), 0.88 (t, J = 6.70 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 143.44, 131.53, 131.49, 128.45, 128.29, 128.04, 123.49, 120.34, 89.58, 88.69, 35.91, 31.92, 31.25, 29.70 (× 4C), 29.66 (× 5C), 29.57, 29.48, 29.36, 29.25, 22.69, 14.12. IR (KBr) 2918, 2848, 2359, 1463, 751, 723, 688 cm⁻¹. Anal. Calcd. for C₃₂H₄₆: C, 89.24; H, 10.76. Found: C, 89.09; H, 10.97.

2.2.4. Poly[1-(4-Octadecylphenyl)-2-phenylacetylene] (1)

Polymerization of **5** was carried out under dry nitrogen using the following conditions: $[M]_0 = 0.16$ M, $[TaCl_5] = 20$ mM, $[n-Bu_4Sn] = 40$ mM, in toluene at 80 °C for 48 h. The polymerization procedure was as follows. A monomer solution was prepared in a two-necked flask by mixing **5** (210 mg, 0.49 mmol) and toluene (1.29 mL). Another two-necked flask was charged with TaCl₅ (21.5 mg, 0.06 mmol), *n*-Bu₄Sn (39 µL, 0.12 mmol), and toluene (1.5 mL), and the catalyst solution was aged at 80 °C for 15 min. The monomer solution was then added to the catalyst solution and stirred at 80 °C for 48 h. The polymerization was quenched by adding a small amount of methanol. The polymerization mixture was diluted with toluene and poured into methanol while stirring to precipitate the resulting polymer, **1**, as yellow solid. The polymer was isolated by filtration and dried. The polymer yield was determined to be 78% by gravimetry.

2.3. Instruments

¹H and ¹³C NMR were recorded on a Varian 400-MR spectrometer, while infrared spectra were recorded on a JASCO FT/IR-4200 spectrometer. Number-average molecular weight (M_n) and



Scheme 1. Synthesis of 1.

weight-average molecular weight (M_w) were determined by gel permeation chromatography (GPC) calibrated with polystyrene standards using a JASCO liquid chromatography system consisting of PU-2080, DG-2080-53, CO-2060, UV-2070, and two polystyrene gel columns (Shodex KF-806L × 2, eluent: THF). UV–visible absorption and PL emission spectroscopy were performed on JASCO V-650 and JASCO FP-6500 spectrophotometers, respectively. Thermogravimetric analysis (TGA) was conducted using TA Instruments Q500. Differential scanning calorimetry (DSC) was performed using TA Instruments Q2000 in pure nitrogen gas at heating and cooling rates of 10 °C min⁻¹. The PL quantum yields (PLQYs) of the polymer solutions were determined relative to a quinine sulfate solution in 1 N H₂SO₄ when excited at 365 nm (PLQY = 54.6%), and those of the polymer films were obtained relative to 9,10-diphenylanthracence in a poly(methyl methacrylate) matrix (PLQY = 83%).

3. Results and discussion

Polymer **1** was synthesized as shown in Scheme 1 following the method described in the experimental section. For comparison, polymer **2** was also synthesized according to a method reported in a previous study [8]. These polymers had extremely high weight-average molecular weights of 1.52×10^6 (PDI: 2.3) and 8.70×10^5 (PDI: 1.3) g mol⁻¹, respectively. The polymers were hydrophobic owing to the aromaticity of the polyene backbone and the pendant phenyl rings combined with the hydrophobic wrapping effect of the alkyl side chains. Both polymers dissolved easily in common organic solvents such as toluene (solubility parameter, $\delta = 18.3$), THF ($\delta = 18.5$), and chloroform ($\delta = 18.7$). On the other hand, the

polymers did not dissolve in polar organic solvents such as DMF (δ = 24.7) and *n*-propanol (δ = 24.9). When spin-coated onto glass slides, highly transparent films with smooth surfaces were obtained.

Fig. 2a shows the TGA curves of the two polymers. For **1**, weight loss began in earnest at around 420 °C with a conversion point appearing at around 500 °C, with the polymer finally leaving 36 wt % of black ash as a residue at 600 °C. The reason for the conversion point during the thermal degradation was likely due to the long alkyl chain beginning to burn out of the polymer at a lower temperature while the main chain decomposed at a higher temperature. On the other hand, for polymer **2** degradation began much lower, at approximately 230 °C, and as a result, a smaller amount of residue (32 wt%) remained at 600 °C. The relatively significant degradation in **2** could be ascribed to the fact that the Si–C bond in the silylene linkage can be readily cleaved through β -hydrogen elimination during the thermal decomposition [11].

The two polymers were quite soft compared to most PDPA derivatives carrying short alkyl chains because of the plasticizing effect of the longer alkyl chains [3]. However, polymer **1** seemed to be slightly stiffer than **2** in tactile testing. To explain the difference between the mechanical features in more detail, we investigated the thermodynamic properties of the polymers using DSC analysis. Fig. 2b shows the DSC thermograms of the two polymers. Polymer **1** exhibits a thermodynamic phase transition at around 21 °C during the heating process due to an endothermic volume change, while **2** has a much lower transition temperature of 3.1 °C. These endothermic peaks could be ascribed to local relaxation of the long alkyl side chains, namely, the melting of the crystallized alkyl side chains



Fig. 2. a) TGA and b) DSC thermograms (heating rate: $10 \degree C \min^{-1}$ in N₂ atmosphere) of 1 (solid line) and 2 (dotted line).



Fig. 3. a, b) UV-visible absorption and c, d) PL emission spectra (excited at 420 nm) of **1** (solid lines) and **2** (dotted lines) in solution $(1.0 \times 10^{-5} \text{ M in toluene})$ (a, c) and as ~200 nm thick films (b, d).

in part, because other PDPA derivatives having no long alkyl chains exist in glassy states in the temperature range examined here. On the other hand, during the cooling process the polymers showed exothermic changes at lower temperatures (10.3 °C for 1 and $-7.2 \circ C$ for **2**) due to the crystallization of the alkyl side chains. These transition temperatures are much lower than that of the corresponding paraffin wax, octadecane, which has a melting temperature (T_m) of 32 °C. This would be a result of the reduced regularity of the peripheral alkyl chains, which are attached to the amorphous, randomly arranged backbone. Moreover, the enthalpies of fusion (ΔH_{fus}) of the polymers were determined to be 19.0 and 12.3 J g⁻¹, respectively, whereas the ΔH_{fus} of octadecane is 241.6 $|g^{-1}$. Consequently, the crystallinities of the alkyl side chains within the polymers were significantly reduced to 15.5 and 10.3%, respectively, confirming the plasticizing effect on the mechanical features. It should be also noted that 1 maintained the crystallinity of the long alkyl side chains slightly better than **2**, explaining why the former was slightly stiffer than the latter. The difference in the crystallinities of the alkyl side chains of the two polymers was probably due to the Si-C bond in the silylene linkage having a greater torsional angle than the C–C bond, i.e., the alkyl side chains with silylene linkages were arranged more randomly than those without silylene linkages.

Both polymers were quite emissive both in solution and in the solid state. To investigate the photophysical properties in more detail, comparative spectroscopic analysis was conducted. Fig. 3 shows the UV–visible absorption and PL emission spectra of the polymers in solution and as films. The results are also summarized in Table 1. Polymer 1 shows the typical dual absorption maxima

 $(\lambda_{max, abs})$ that characterize PDPA derivatives, with the maxima appearing at 369 and 428 nm in solution and 376 and 428 nm in film. The spectra of **2** are very similar (dual $\lambda_{max, abs}$ at 375 and 432 nm in solution and 380 and 432 nm in film), although the absorption bands are slightly shifted to longer wavelengths. This indicates that the silvlene linkage weakly but clearly influenced the electronic structure of the polymer backbone in the ground state. Similarly, polymer 1 shows shorter PL emission wavelengths than 2. In solution, **1** exhibits a maximum PL wavelength ($\lambda_{max, PL}$) of around 485 nm together with a shoulder at around 505 nm, while the maximum and the shoulder band are inverted in 2. As films, the λ_{max} , PL of the two polymers appear at the same wavelength, 517 nm, while the shoulders both appear at wavelengths close to 480 nm. This indicates that the silvlene linkage had almost no effect on the energy levels of the electronic transitions. However, the relative intensity of the shoulder is slightly greater in 1 than it is in 2. Indeed, the PLQYs of 1 were 63.1 and 27.4% in solution and as a

Table 1	
Photophysical properties of 1 and 2.	

Polymer	In solution ^a			As films (spin coating)		
	λ _{max, abs}	λ _{max, PL} ^b	PLQY ^c	λ _{max, abs}	λ _{max, PL} ^b	PLQY ^c
	[nm]	[nm]	[%]	[nm]	[nm]	[%]
1	369, 428	485, 502	63.1	376, 428	487, 517	27.4
2	375, 432	486, 505	49.4	380, 432	488, 517	20.6

^a 1.0×10^{-5} M in toluene.

^b Excited at 420 nm.

^c Determined using the reference point method as described in the experimental section.



Fig. 4. Plots of PL intensity ratio (I/I_0 , where I_0 is PL intensity at 20 °C) of **1** (solid) and **2** (blank) as a function of temperature from 20 to 60 °C (excited at 420 nm, monitored at maximum PL wavelengths). a) Solutions (1.0×10^{-5} M in toluene), and b) Films (spin-coated, thicknesses of ~200 nm).

film, respectively, with these values being greater than those of **2** (49.4% in solution, 20.6% as a film). This indicates that the **1** restricts non-radiative emission decay more efficiently at ambient temperature than **2**. This is probably because the alkyl side chains without silylene linkages in **1** restrain the vibrational relaxation in the excited state more efficiently than the chains with silylene linkages in **2**. This seems to be closely related to the differences in the thermodynamic local relaxations of the two polymers as observed using DSC.

To verify the relationship between PL emission and thermodynamic properties, the PL quenching behaviors of the two polymers on heating were compared. Fig. 4 shows the PL intensity ratios of the two polymers between 20 and 60 °C at 5 °C increments in solution and as films (see the temperature-variable PL emission spectra in Fig. S1). As is usually the case for fluorophores, the PL intensity showed considerable temperature dependence. The PL intensities of both polymers significantly decreased with increasing temperature. This PL quenching was likely due to thermallyinduced molecular perturbation [12]. However, as expected there was a slight difference in the PL quenching rates. The PL intensity ratio of 1 in solution at 60 °C was approximately 0.59, which is slightly higher than that of **2** at the same temperature (0.46). This indicates a lower PL quenching rate for 1 compared to 2. This could be due to the greater restriction of vibrational relaxation in **1** relative to 2. A similar tendency was also observed in films. Consequently, the absence of silvlene linkages in PDPA derivatives is more favorable for producing more thermodynamically stable polymers with higher PL quantum efficiencies.

PL emission spectra of the polymers were also measured below 20 °C because it was thought that a conversion point, i.e., a critical PL change, may occur at around the phase transition temperature of 21 °C especially for **1**. Contrary to our expectation, however, the PL change at near 20 °C was not so pronounced during the cooling process from 60 °C to 0 °C (Fig. S2). It is probably because **1** completely lost its crystallinity owing to the abruptly quenched, randomly arranged polymer chain structure originating from the spin-coating method [13,14]. On the other hand, a critical PL change was clearly seen at near 20 °C for **1** in a solvent-cast film during the cooling process (Fig. S3). It is presumably because the polymer chains are rearranged into a certain ordered form in part via the slow evaporation of solvent during the film preparation process, imparting crystallinity to the long alkyl side chains [13,14]. However, **2** did not show such critical PL change in the solvent-cast film

because the phase transition temperature is much lower than the temperature range tested in this study, namely, the alkyl side chains exist as being melt throughout the temperature range. This indicates that the thermodynamic PL emission behavior of the polymers is dependent on the feature of film according to the preparation method as well.

4. Conclusions

We successfully synthesized a PDPA derivative, **1**, bearing a long alkyl side chain without a silylene linkage and compared with the corresponding polymer with a silylene linkage, **2**. Both polymers dissolved in common organic solvents such as toluene and THF, but did not dissolve in polar solvents owing to their intrinsic hydrophobicity. Transparent films with good features were obtained from the solutions. Polymer **1** was more thermally stable than **2** owing to the absence of Si–C bonds. It was also slightly stiffer than **2** owing to the increased temperature required for local relaxation and the higher crystallinity imposed by the more restricted motion of the alkyl side chains. Polymer **1** was more emissive than **2** for the same reason. Our results will be helpful for developing thermally resistant, thermodynamically stable, and highly emissive PDPA derivatives for advanced functions and applications.

Acknowledgements

This work was supported by the Basic Science Research Program of National Research Foundation of Korea (NRF) grants funded by the Korea government (MEST) (2014R1A2A1A11052446).

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.polymer.2017.07.011.

References

- Y.-J. Jin, G. Kwak, Properties, functions, chemical transformation, nano-, and hybrid materials of poly(diphenylacetylene)s toward sensor and actuator applications, Polym. Rev. 57 (2017) 176–200.
- [2] W.-E. Lee, J.-W. Kim, C.-J. Oh, T. Sakaguchi, M. Fujiki, G. Kwak, Correlation of intramolecular excimer emission with lamellar layer distance in liquidcrystalline polymers: verification by the film-swelling method, Angew. Chem. Int. Ed. 49 (2010) 1406–1409.
- [3] Y.-J. Jin, J.-E. Bae, K.-S. Cho, W.-E. Lee, D.-Y. Hwang, G. Kwak, Room

temperature fluorescent conjugated polymer gums, Adv. Funct. Mater 24 (2014) 1928–1937.

- [4] Y.-J. Jin, J.-H. Yoon, T. Sakaguchi, C.-L. Lee, G. Kwak, Highly emissive, waterrepellent, soft materials: hydrophobic wrapping and fluorescent plasticizing of conjugated polyelectrolyte via electrostatic self-assembly, Adv. Funct. Mater 26 (2016) 4501–4510.
- [5] W.-E. Lee, C.-J. Oh, G.-T. Park, J.-W. Kim, H.-J. Choi, T. Sakaguchi, M. Fujiki, A. Nakao, K. Shinohara, G. Kwak, Substitution position effect on photoluminescence emission and chain conformation of poly(diphenylacetylene) derivatives, Chem. Commun. 46 (2010) 6491–6493.
- [6] K. Tsuchihara, T. Masuda, T. Higashimura, Tractable silicon-containing poly(diphenylacetylenes): their synthesis and high gas permeability, J. Am. Chem. Soc. 113 (1991) 8548–8549.
- [7] Y. Hu, M. Shiotsuki, F. Sanda, T. Masuda, Synthesis and extremely high gas permeability of polyacetylenes containing polymethylated indan/tetrahydronaphthalene moieties, Chem. Commun. (2007) 4269–4270.
- [8] G. Kwak, M. Minaguchi, T. Sakaguchi, T. Masuda, M. Fujiki, Poly(diphenylacetylene) bearing long alkyl side chain via silylene Linkage: its lyotropic liquid crystallinity and optical anisotropy, Chem. Mater 19 (2007) 3654–3661.

- [9] Z. Peng, A.R. Gharavi, L. Yu, Synthesis and characterization of photorefractive polymers containing transition metal complexes as photosensitizer, J. Am. Chem. Soc. 119 (1997) 4622–4632.
- [10] H.-F. Chow, C.-W. Wan, K.-H. Low, Y.-Y. Yeung, A highly selective synthesis of diarylethynes and their oligomers by a palladium-catalyzed sonogashira coupling reaction under phase transfer conditions, J. Org. Chem. 66 (2001) 1910–1913.
- [11] G. Kwak, T. Masuda, Synthesis and thermal properties of regio- and stereoregular poly(silylene-1,4-phenylenevinylene)s, Macromol. Rapid Commun. 22 (2001) 1233–1236.
- [12] G. Kwak, S. Fukao, M. Fujiki, T. Sakaguchi, T. Masuda, Temperature-dependent, static, and dynamic fluorescence properties of disubstituted acetylene polymer films, Chem. Mater 18 (2006) 2081–2085.
- [13] Y.-J. Jin, W.-E. Lee, C.-L. Lee, G. Kwak, Highly emissive 'Frozen-In' conjugated polymer nanofibers, Soft Matter 12 (2016) 4443–4448.
 [14] D.-H. Han, W.-E. Lee, S.-J. Kim, S.-D. Park, G. Kwak, Solvent-driven reorgani-
- [14] D.-H. Han, W.-E. Lee, S.-J. Kim, S.-D. Park, G. Kwak, Solvent-driven reorganization of poly(diphenylacetylene) in film and nanofibers by means of swelling method: solvent annealing effects on fluorescence emission properties and microstructures, Polym. Bull. 69 (2012) 49–61.