SINTHESIS OF NONCONJUGATED TADF POLYMERS WITH DIFFERENT MAIN CHAINS

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Abstract

Polysiloxane and polystyrene main-chain polymers were synthesized and investigated that contain the same side chains from the moieties responsible for thermally activated delayed fluorescence (TADF) at different ratios. It was shown that the polysiloxane and polystyrene main-chain polymers can be obtained from the same TADF monomers by polymer analogues reactions of hydrosilylation with polymethylsilane PMS-60 or by free-radical polymerization, respectively. Each of the polymers obtained was characterized using gel permeation chromatography (GPC) and thermogravimetric analysis (TGA). The general conclusions of the comparative studies of the polymers are presented.

Key words: TADF polymers, polystyrene, polysiloxane, molecule designing.
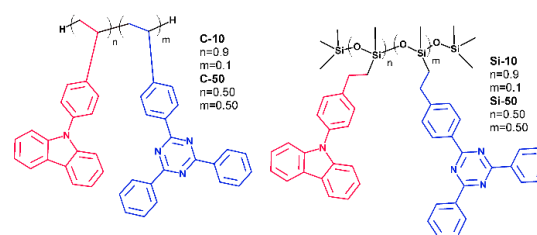
Introduction

Modern displays based on organic light-emitting diodes (OLEDs) are commonly used in the production of diverse devices. Despite some fundamental principles, their performance is restricted. These limits are performance level, period of use, and thermal stability. One of the improvements is a transition from OLEDs to polymer light-emitting diodes (PLEDs) with thermally activated delayed fluorescence which can break off the external quantum efficiency (EQE) constraint and impart better device lifetimes. The main TADF feature is spatially separated HOMO/LUMO levels, which are located at a donor/acceptor (DA) pair that possesses small energy gap (ΔE_{ST}) between the lowest singlet (S_1) and triplet (T_1) states. This architecture determines the powered reverse intersystem crossing (RISC) and allows for improving the performance. Research efforts in this field have afforded the DA pairs like acridan/triphenyltriazine, dibenzothiophene/dibenzosulfoxide, phenoxazine/2,5-diphenyl-1,3,4-oxadiazole [1–3]. However, simultaneous works directed to reveal polymer architecture features have demonstrated the ability to bring chromophores closer to each other, which can lead to the aggregation induced quenching or aggregation induced emission. The latter is used to avoid the conjugation between the donor and acceptor moieties, achieve low ΔE_{ST} by preventing the donor–acceptor interaction, and design TADF polymers with blue emission, which is difficult to reach. The group of F. Wang reported a series of polystyrenes with *N*-phenylacridan (Ac) or 9,9-bis(1,3-di-*tert*-butylphenyl)-10-phenylacridan (TBAc) as the donor and triphenyltriazine as the acceptor pendant groups which demonstrate the advantages of polymers with Ac donor: high (51–60%) film state photoluminescence quantum yield, very

low ΔE_{ST} (less than 0.021 eV), blue emitting color, and EQE of 121% for the Ac-donor polymer with 5% acceptor content. This result shows an opportunity to create a blue polymer *via* space separation of donor–acceptor units. This approach allowed for developing wide range emission [4]. The studies on the main-chain nature of the conjugated TADF polymers revealed the acceleration of RISC by external heavy-atom effect [5]. There are well studied materials based on a non-conjugated architecture with carbazole as a host functional unit and diverse TADF units, but the non-conjugated polymers with DA pendant groups are less investigated [6, 7]. Therefore, this work was aimed at the synthesis of TADF polymers for further study of the effect of the main chain nature on the electroluminescence and thermal properties. The structures varied between a polystyrene and polymethylsiloxane backbone with the acceptor content from 5% to 50%.

Results and discussion

The synthetic route was divided into two parts: the preparation of styrene-like precursors (Scheme 1) and target polymers (Scheme 2). 9-(4-Ethenylphenyl)-carbazole (ST-P-CZ) was obtained by the Buchwald–Hartwig reaction under different conditions: 1) refluxing at 100 °C, 3h, 2) stirring at 105 °C, 3 h, MW(55W). This approach is based on the previously published techniques [8]. The application of a microware reactor afforded a dramatical increase in the reaction yield from 40 to 82%. Flash chromatography in toluene and column chromatography in cyclohexane were used as separation techniques. 2-(4-Vinylphenyl)-4,6-diphenyl-1,3,5-triazine (ST-2P-TRZ) was obtained by several methods. The successful scheme included the sequential substitution of cyanuric cloride with 4-

bromostyrene followed by the Suzuki reaction with phenylboronic acid. This approach was described elsewhere [9]. However, the corresponding products appeared to be self-polymerized to some extent during the processing and storage, which decreases the yield of the isolated product.
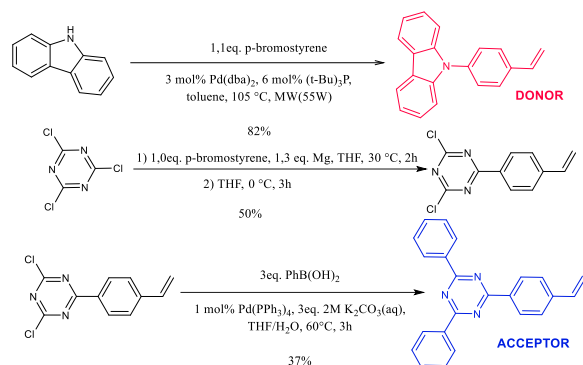
Scheme 1. Synthesis of the precursors.
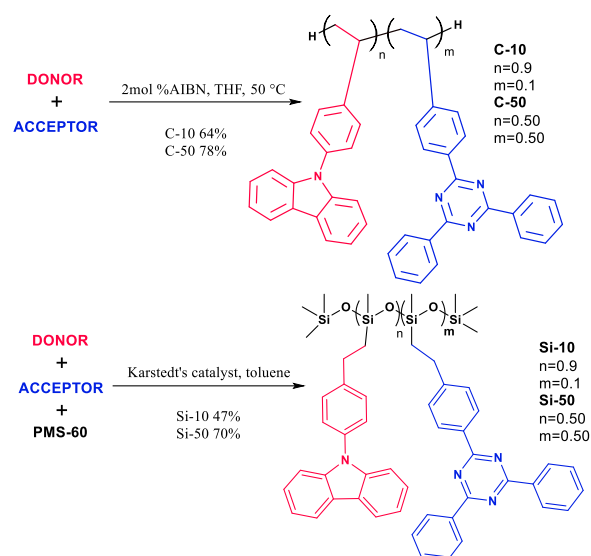
Scheme 2. Synthesis of the target polymers.

For comparison, two polymers with a polystyrene main chain (C-10, C-50) have been synthesized by the free-radical polymerization (Scheme 2). The polymers with a polymethylsiloxane main chain (Si-10, Si-50) were prepared through the hydrosilylation addition of the precursors to commercially available PMS-60 (Scheme 2). To separate the low-molecular-weight admixtures, a precipitating technique was used. The content of these admixtures was determined by GPC.

The molecular weight characteristics of the polymers obtained were determined by GPC relative to polystyrene standards. The molecular weight distributions of the polysiloxane derivatives are in agreement with grafting to PMS-60 (Table 1). The values of M_w and M_n of C-50 differ from those of the others due to the peculiarities of the free-radical polymerization. Despite the difference in molecular masses, the polydispersity indices (PDI) for all samples were above 2.0.

The TGA data for the polymers with the same type main chain appeared to be very similar (Table 2). The polystyrene main-chain polymers demonstrated 5 wt % loss at the temperatures above 314 °C in the air and above 374 °C under

Table 1. Molecular weight characteristics of the polymers

Polymer	Molecular weight characteristics		
	M_n, kDa	M_w, kDa	PDI
Si-10	22.1	50.8	2.30
Si-50	26.4	73.9	2.80
C-10	22.2	60.1	2.71
C-50	119.2	331.0	2.78

Table 2. Results of thermogravimetric analysis

Polymer	5 wt % loss, °C	
	Air	Ar
Si-10	348	404
Si-50	355	405
C-10	319	379
C-50	314	374

argon, indicating their high thermal stability. The polysiloxane main-chain polymers displayed improved thermal stability: above 348 °C in the air and above 404 °C under argon.

Conclusions

The synthetic route to the TADF polymers with polystyrene and polysiloxane main chains was elaborated. The molecular weight distributions are in good agreement with the literature data for *N*-(3-ethenylphenyl)acridan and 2-(3-vinylphenyl)-4,6-diphenyl-1,3,5-triazine copolymers [10]. The polymers with the polysiloxane backbone were obtained in lower yields, but feature more reproducible molecular weight properties and better thermal stability in comparison to the polystyrene analogs. The TADF characterization with the fluorescence kinetic studies will be presented in due course.

Acknowledgements

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Electronic supplementary information

Electronic supplementary information (ESI) available online: the experimental section, NMR and MALDI spectra, thermal data. For ESI, see DOI: 10.32931/ioXXXXx.

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