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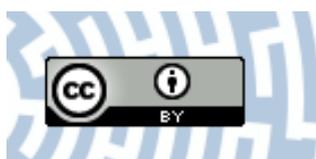
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ORIGINAL PAPER

Novel concept of polymers preparation with high photoluminescent quantum yield

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Abstract A series carbazolyl-containing polymers were synthesized by anionic polymerization of various oxiranes and methyl methacrylate. The polymerization was carried out using as initiator carbazylpotassium activated 18-crown-6 in THF. The polymers were prepared and found using size exclusion chromatography to have a degree of polymerization (DP_n) about 20 relatively and low dispersity in the range of 1.07–1.66. Their optical properties were investigated by means of UV–vis and photoluminescence spectroscopies. The obtained polymers emitted light with maximum emission about 370 nm and high quantum yield ranging up to 79 %. Thus, it was confirmed that the utilization of fluorophore initiator for polymerization of non photoresponsive monomers is quite efficient for the preparation of photoluminescent polymers.

Introduction

Photoluminescent materials have been developed for more than 50 years and attracted attention for their applications [1]. However, new organic light-emitting materials (OLED) with high luminescence efficiency, little self-quenching, good carrier transporting property, and high stability are still desirable. Carbazole-based materials, both low molecular weight compounds and polymers, have been used as good electro- and optical-active materials due to their holetransporting capabilities and strong

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fluorescence [2–13]. For example, luminescent properties of carbazyl-containing quinacridone derivatives [5] and phenol-pyridyl boron complexes [3] of tolan derivatives [3] have been noted. Moreover, several new efficient luminescent materials with a carbazole unit have been reported [6–13], e.g., materials containing benzothiadiazole and two carbazole units showed a significant increase in the emission intensity and quantum efficiency (75 %) [6], a group of fluorene derivatives with carbazole units was utilized as emitters for the construction of blue organic light emitting diodes (OLEDs) [12] and light-emitting spirobifluorene materials containing two carbazole moieties demonstrated efficient and stable bright red or green phosphorescence OLEDs [13]. Furthermore, a novel luminescent platinum(II) complex of porphyrin with end-capped carbazole tails was used as an optical oxygen sensor with a high response rate [7–9], while an europium(III) complex with carbazole involving both hole- and electron-transporting functional groups has been used as a red light-emitting material in OLEDs [11]. Macromolecules end-capped carbazole moieties were also used as luminescent films electrodeposited (ED) with good electropolymerization behaviors and properties [10]. Likewise, polymers bearing carbazole structure has been widely described [14–19], e.g., fluorescent carbazolyl-labeled polysiloxanes [14]. A green light-emitting phosphorescent and polymeric light-emitting diode (PLED), containing a layer of a carbazole-oxadiazole copolymer showed a high efficiency, current densities, and luminance levels [15]. New electroactive polymers with carbazole conjugated—aliphatic nonconjugated repeating units in the main chain have been reported. [16]. High, blue photoluminescence activity of segmented polyethers containing oxadiazole/carbazole units and flexible aliphatic moieties have also been described [17, 18]. Furthermore, nonconjugated hybrids of carbazole and fluorine have been investigated as a novel host material for highly efficient phosphorescent OLEDs [19].

Carbazole polymers have previously been prepared from cyclic monomers, that is, carbazolyl—substituted oxiranes [20–24]. In this work, we proposed a new idea for the synthesis of photoluminescent polymers based on utilizing as a polymerization initiator a compound bearing a carbazolyl group and prepared a range of carbazole polymers. The potassium salt of carbazole activated 18-crown-6 was applied for the polymerization of methyl methacrylate and several monosubstituted oxiranes, namely, propylene oxide, 1,2-butylene oxide, styrene oxide, allyl glycidyl ether, isopropyl glycidyl ether, and phenyl glycidyl ether. Comparatively, the polymerization of (9-carbazolylmethyl)oxirane was carried out to obtain the polymer containing fluorophore in each repeating unit. The photoluminescence (PL) of prepared polymers was tasted in solutions, and PL quantum yield was determined using an integrating sphere.

Experiment

Materials

Tetrahydrofuran, 99 % (Acros Organics) was dried over CaH_2 (Aldrich) and distilled at 66 °C. 18-Crown-6, 98 % (Aldrich) was used without purification.

Carbazole, 97 % (Aldrich) was purified by crystallization from methanol. Potassium *t*-butoxide, 1.0 mol/dm^3 solution in tetrahydrofuran (Aldrich) and methyl iodide (Aldrich) were used without purification. Potassium hydride, 30 wt% dispersion in mineral oil (Aldrich) was mixed with *n*-pentane (Acros Organics) in a dry argon atmosphere and then decanted. It was repeated three times followed by a threefold washing with dry tetrahydrofuran. Finally, the product was dried in vacuum. The KH present was determined by a standard gas low calculation of the hydrogen liberated after treating with 2-butanol (1.0 H_2 = 1.0 KH). The resulting solution was titrated to a phenolphthalein end point. Very little excess (<1 %) of total base over hydride base (from gas evolution) indicated small hydrolysis of the original KH sample [6]. Propylene oxide, 99 % (Aldrich), 1,2-butylene oxide, 99 % (Aldrich), styrene oxide, 97 % (Aldrich), allyl glycidyl ether, 99 % (Aldrich), isopropyl glycidyl ether, 98 %, (Aldrich), phenyl glycidyl ether, 99 % (Aldrich) and methyl methacrylate, and 99 % (Aldrich) were dried with CaH_2 and distilled at 34, 63, 194, 154, 131, 245, and 100 °C, respectively. (9-Carbazolylmethyl)oxirane (Biolar, Latvia) was crystallized twice from toluene (99 %), yielding a product with a melting point of 113 °C.

Synthesis of carbazylpotassium activated 18-crown-6 (18C6)

Carbazylpotassium was prepared by the reaction of potassium hydride with carbazole. Tetrahydrofuran (15 cm^3), potassium hydride (0.08 g), 18-crown-6 (0.528 g, 0.002 mol), and carbazole (0.33 g, 0.002 mol) were introduced into a glass reactor (50 cm^3) equipped with Teflon valve and magnetic stirrer and mixed during 1 h. A stoichiometric amount of hydrogen (44.7 cm^3) was evolved in the reaction resulting in the formation of the white powder of the product. The reaction course was shown on Scheme 1.

Polymerization procedure

Monomers, i.e., propylene oxide (2.8 cm^3), 1,2-butylene oxide (3.5 cm^3), styrene oxide (4.6 cm^3), isopropyl glycidyl ether (5.0 cm^3), allyl glycidyl ether (4.8 cm^3), phenyl glycidyl ether (4.0 cm^3), or methyl methacrylate (4.3 cm^3) were added to the suspension of initiator obtained in tetrahydrofuran. The reaction mixture was then mixed for 2 weeks. After total conversion of the monomer, obtained by chromatography method, methyl iodide (0.2 cm^3) was introduced to the system to transform active centers of chain growth to methoxy or methyl groups. Next, the precipitate of KI/18C6 was decanted, and the solvent was evaporated under reduced

Scheme 1 Synthesis of carbazylpotassium in the presence of 18-crown-6 complexing agent

pressure. By mixing a polymer with $CHCl_3/H_2O$ (50 cm^3/50 cm^3), system two layers were formed: a lower layer containing polymer solution in $CHCl_3$ and an upper containing water and the potassium salt residue. After evaporation of $CHCl_3$, the polymer was diluted in *n*-pentane. Traces of carbazole residue which is insoluble in hydrocarbon were removed by centrifugation. Then, the solvent and other organics were removed from polymer by distillation at 100 °C/10^{-3}Torr. This method of purification was applied for polymers of propylene oxide, 1,2-butylene oxide, isopropyl glycidyl ether, and allyl glycidyl ether.

In a separate experiment polymerization of (9-carbazolylmethyl), oxirane initiated potassium *t*-butoxide in tetrahydrofuran was carried out. Tetrahydrofuran (15.6 cm^3) and 1.0 mol/dm^3 solution of initiator (0.8 cm^3) were placed in the reactor and then monomer (3.6 g) was added. After the appropriate time of mixing (3 weeks), polymerization was stopped by the addition of methyl iodide (0.2 cm^3), and the polymer was precipitated with methanol. The same method was used for poly(phenyl glycidyl ether) and poly(methyl methacrylate).
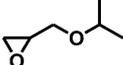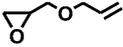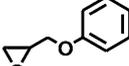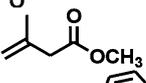
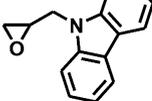## Measurements

100 MHz ^{13}C NMR spectra were recorded in CDCl$_3$ at 25 °C on a Bruker Avance 400 pulsed spectrometer equipped with a 5 mm broadband probe and applying Waltz16 decoupling sequence. Chemical shifts were referenced to tetramethylsilane serving as an internal standard. To obtain a good spectrum of the polymer, main chain exhibiting its microstructural details about 3000 scans was satisfactory, but to observe the signals of the polymer chain ends, more than 10,000 scans were necessary. Molar masses and dispersities of polymers were obtained by means of size exclusion chromatography (SEC) using a Shimadzu Prominance UFLC instrument at 40 °C with a Shodex 300 mm × 8 mm OHpac column using tetrahydrofuran as solvent. Polystyrene (Acros Organics, 99 %) were used as calibration standards. UV–vis absorption spectra were recorded using a Lambda Bio 40 Perkin Elmer spectrophotometer. The photoluminescent (PL) spectra were obtained on a VARIAN Cary Eclipse Fluorescence Spectrophotometer. The quantum yields of fluorescence were determined by an absolute method at room temperature, using the integrating sphere with the solvent as a blank. The solutions of samples were first filtered and diluted to an absorbance less than 0.1 to avoid the inner filter effect and influences of impurities from the medium and then excited at the wavelength corresponding to the excitation wavelength of the polymer.

Results and discussion

The anionic polymerization of propylene oxide, 1,2-butylene oxide, styrene oxide, isopropyl glycidyl ether, allyl glycidyl ether, phenyl glycidyl ether, methyl methacrylate, and (9-carbazolylmethyl)oxirane results in polymers denoted as P1, P2, P3, P4, P5, P6, P7, and P8, respectively (cf. Table 1). The polymers P1–P7 were prepared using carbazylpotassium activated 18-crown-6 as initiator. It should be stressed that the fluorophore unit in these polymers comes only from the initiator.

Table 1 Number-average molecular weight (M_n) and dispersity (M_w/M_n) measured by SEC, the calculated molecular weight (M_n^{calc}), yield and polymerization degree (DP_n) of synthesized polymers

No	Polymer	Monomer	M_n^{calc}	M_n	M_w/M_n	Yield, %	DP_n
P1	poly(propylene oxide)		1160	1300	1.20	98.6	22
P2	poly(1,2-butylene oxide)		1440	1400	1.05	99.0	19
P3	poly(styrene oxide)		2400	2200	1.16	98.9	18
P4	poly(isopropyl glycidyl ether)		2320	2300	1.07	98.7	20
P5	poly(allyl glycidyl ether)		2280	2400	1.09	99.4	21
P6	poly(phenyl glycidyl ether)		3000	2700	1.34	98.0	18
P7	poly(methyl methacrylate)		2000	2100	1.66	99.2	20
P8	poly((9-carbazolylmethyl)oxirane)		2230	660	1.02	69.1	3

Poly (9-carbazolylmethyl)oxirane (P8) bearing a carbazoyl structure in each polymer repeating unit was prepared for comparison.

Synthesis and characterization

In the polymerizations, all monomers except those of (9-carbazolylmethyl)oxirane the initial monomer, and initiator concentrations were 2.0 and 0.1 mol/dm³, respectively. Polymerization of the latter was initiated with potassium *t*-butoxide and carried out at the initial monomer and initiator concentration of 0.4 and 0.04 mol/dm³, respectively. It was known from the literature [25, 26] that in the anionic polymerization of monomers 1,2-butylene oxide, isopropyl glycidyl ether, allyl glycidyl ether, and phenyl glycidyl ether the chain transfer reaction to the monomer does not occur. However, in the case of polymerization of propylene oxide and styrene oxide, side reactions take place resulting in the formation of macromolecules with –OH end group (10–15 %) [23, 27, 28]. However, in the case of methyl methacrylate, another type of side reaction occurs during the initiation, i.e., acyl-oxygen bond cleavage (14 %) resulting in macromolecules with CH_3O-starting groups [29, 30]. The chemical structure of synthesized polymers was confirmed by ¹³C NMR. ¹³C NMR spectra of polymers P1-P7 revealed the presence of starting carbazolyl group in macromolecules (109.2, 118.9, 120.2, 122.9, 125.6, and 140.8 ppm) (Fig. 1). They are, for example, signals of unsaturated *cis-*
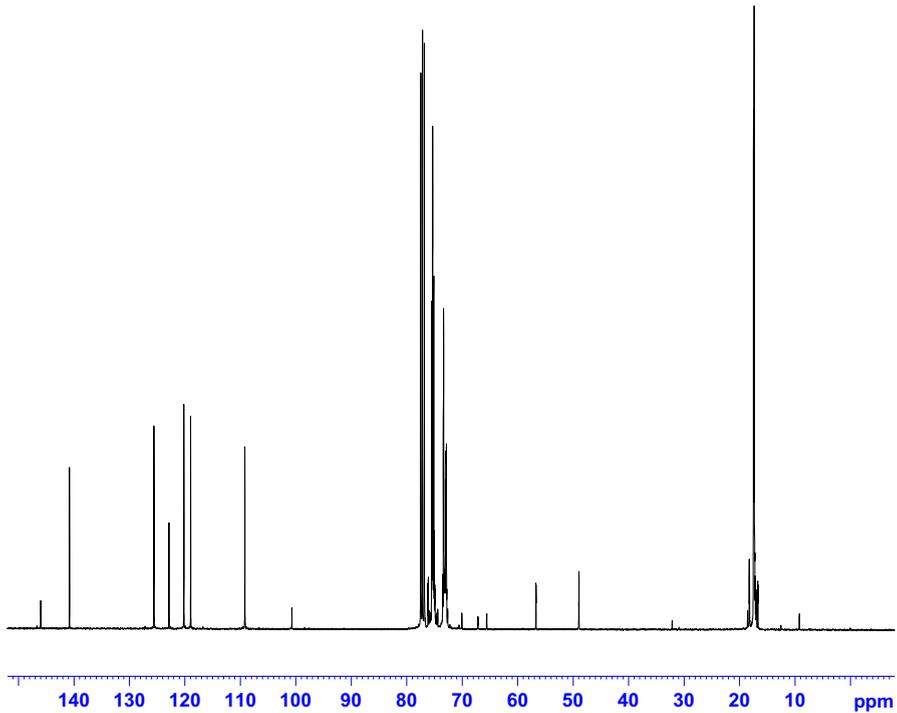
Fig. 1 ^{13}C NMR spectrum of poly(1,2-propylene oxide)(P1) synthesized in the presence of carbazylpotassium

propenyloxy groups (100.7, 146.0 ppm) in polymer P1,(136.4, 159.7 ppm) in polymer P3 and 59.1 ppm of methoxy group in polymer P7.

Molecular weight of polymers was estimated by size exclusion chromatography (SEC), and the results are collected in Table 1.

The calculated number-average molecular weights (M_n) are similar as estimated by SEC. All polymers showed low molecular weight distribution (M_w/M_n) are in the range of 1.07–1.66. It might results from rapid initiation and high effectivity of initiator. The polymers exhibited a relatively high the degree of polymerization (DP_n) about 20, except for P8. In the polymerization of (9-carbazolylmethyl)oxirane, chain transfer to the monomer dominates and causes, distinct decrease of molar mass of the polymer. Consequently, only oligomers were formed. The course of oxiranes polymerization with carbazylpotassium activated18C6 was shown in Scheme 2.

Optical properties

Optical properties of obtained polymers were investigated by UV–Vis absorption and photoluminescence (PL) spectroscopy. At the beginning of the investigations, the UV–Vis measurements of poly(propylene oxide) (P1) and poly(1,2-butylene
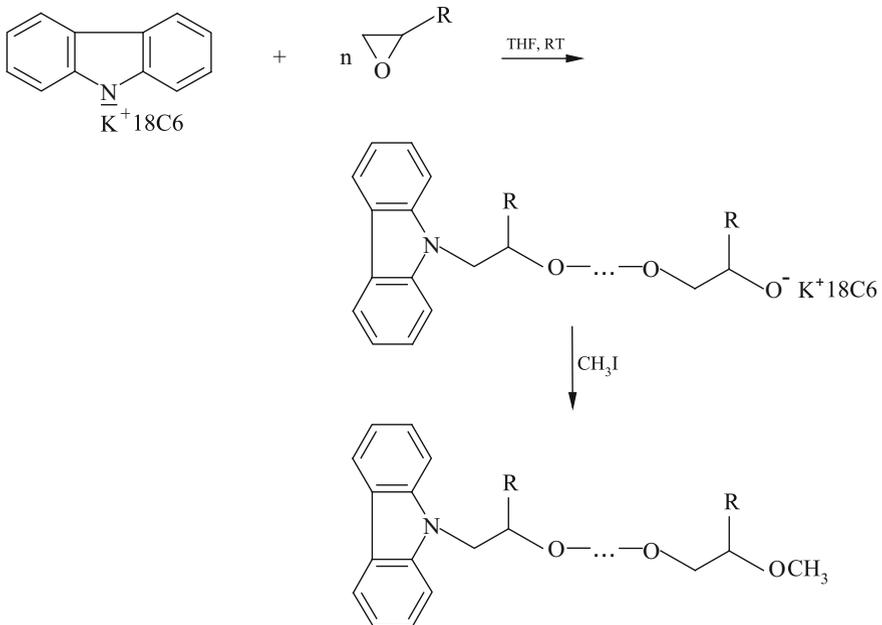
where R: CH₃, CH₃CH₂, CbCH₂, Ph, PhOCH₂, (CH₃)₂CHOCH₂, CH₂=CHCH₂O
(Cb denotes carbazyl group)

Scheme 2 Schematic representation of oxirane polymerization initiated with carbazylpotassium

oxide) (P2) were carried out in two solvents which differ significantly in polarity CHCl$_3$ (dielectric constant (ε) = 4.81) and NMP (ε = 33.0) on 1 × 10^{-4} mol/dm^3 solutions. The lower range of UV–vis measurements was limited by the transparency of the solvent used, that is, 240 nm for CHCl$_3$ and 260 nm for NMP. The UV–vis spectra of P1 and P2 are depicted in Fig. 2a, b.

The electronic absorption spectra of both P1 and P2 in solution are similar and showed two absorption bands with the maximum (λ_{max}) located around 260, 292, and third band of pronounced vibronic structure with two maxima at about 328 and 341 nm. It should be noted that a solvatochromism effect was not observed, despite the striking difference in polarity of the solvents used. The PL spectra for P1 and P2 were recorded also in chloroform and NMP (cf. Fig. 2a, b). The emission intensity significantly decreased as the medium changed from NMP to CHCl$_3$; thus, the optical properties investigations of the other polymers were conducted in NMP solution. As can be seen from Fig. 2c, all polymers showed practically the same absorption properties except for poly(phenyl glycidyl ether)(P6). In the case of this polymer, P6, the differences are seen in the high energy region probably because of the presence of an additional phenyl ring in their structure. The emission spectra of polymers were recorded with a different excitation wavelength (λ_{ex}) to establish λ_{ex} under which polymers give the highest PL intensity, in NMP solutions at concentrations of 1 × 10^{-4} mol/dm^3. The highest emission intensity was obtained
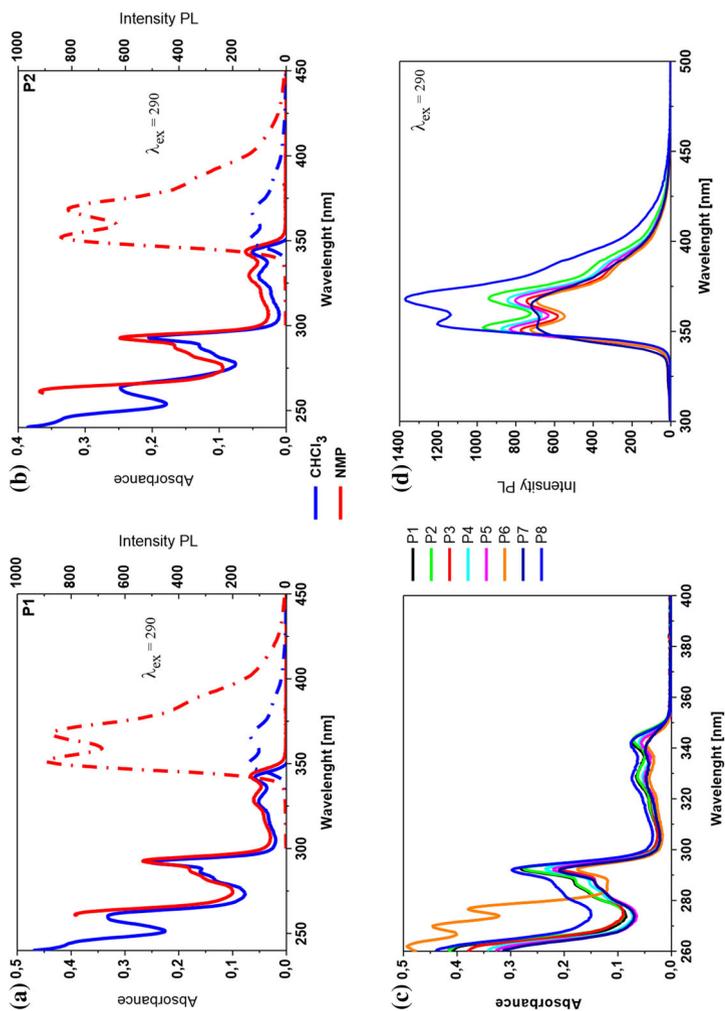
Fig. 2 UV–vis absorption (*solid lines*) and PL (*dash lines*) spectra of P1 (**a**) and P2 (**b**) in CHCl₃ (*blue lines*) and NMP (*red lines*) solutions. **c**, **d** UV–vis absorption (**c**) and PL spectra (**d**) of obtained polymers in NMP solutions. Concentration of all solutions was 1×10^{-4} mol/dm³ (color figure online)
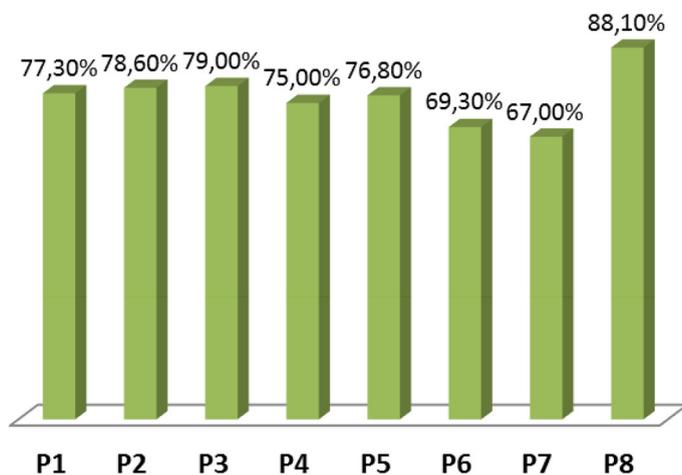
Fig. 3 Quantum yield (Φ_f) of investigated polymers in NMP solution (concentration 1×10^{-4} mol/dm^3, $\lambda_{ex} = 290$ nm)

under $\lambda_{ex} = 290$ nm. The polymers examined under different excitation wavelengths exhibited an emission band, with the maximum (λ_{em}) located in the UV region, around 350 and 367 nm (cf. Fig. 2d).

In the next step of investigations, the PL quantum yield (Φ_f) was estimated using an integrating sphere and the results are presented in Fig. 3.

It should be noticed that all obtained polymers showed a high Φ_f value in the range between 67 and 88 %. The highest PL Φ_f was found for poly((9-carbazolylmethyl) oxirane) (P8), which contains fluorophore moiety in each repeating unit. Considering the polymers containing only a single terminal carbazolyl group coming from the initiator (P1–P7), differences in PL quantum yield from 67 to 79 % were seen. The lowest Φ_f below 70 % exhibited poly(phenyl glicydyl ether) (P6) and poly(methyl methacrylate) (P7).

Conclusions

To summarize, in this study, novel an alternative idea for the synthesis of photoluminescent polymers is presented. In the investigated polymers, the fluorophore units come only from the carbazyl group of initiator, except for P8. The polymers demonstrated emission of light with high PL quantum yield (Φ_f) up to 79 %, which is only 9 % lower than Φ_f of the polymer containing the carbazoyl moiety in each repeating units, that is, poly (9-carbazolylmethyl)oxirane.

References

1. Chen R, Lockwood DJ (2002) Developments in luminescence and display materials over the last 100 years as reflected in electrochemical society publications. J Electrochem Soc 149:S69–S78
2. Okhita M, Endo A, Sumiya K, Nakanotani H, Suzuki T, Adachi C (2011) Photophysical characteristics of 4,4′-bis(N-carbazolyl)tolan derivatives and their application in organic light emitting diodes. J Lumin 131:1520–1524
3. Zhang Z, Yao D, Zhao S, Gao H, Fan Y, Su Z, Zhang H, Wang Y (2010) Carbazolyl-contained phenol-pyridyl boron complexes: syntheses, structures, photoluminescent and electroluminescent properties. Dalton Trans 39:5123–5129
4. Satoh R, Naka S, Shibata M, Okada H, Inoue T, Miyabayashi T (2011) Self-aligned organic light-emitting diodes with color changing by ink-jet printing dots. Jpn J Appl Phys 50:01BC09
5. Zhao GL, Fan Y, Huo C, Bian H, Song WF, Zhang JY, Wang Y (2009) Synthesis, supramolecular structures and luminescent properties of quinacridone derivatives bearing carbazole groups. Chin Sci Bull 54:1677–1684
6. Tao YM, Li HY, Xu QL, Zhu YC, Kang LC, Zheng YX, Zuo JL, You XZ (2011) Synthesis and characterization of efficient luminescent materials based on 2,1,3-benzothiadiazole with carbazole moieties. Synth Met 161:718–723
7. Huo C, Zhang H, Zhang H, Zhang H, Yang B, Zhang P, Wang Y (2006) Synthesis and assembly with mesoporous silica MCM-48 of platinum(II) porphyrin complexes bearing carbazyl groups: spectroscopic and oxygen sensing properties. Inorg Chem 45:4735–4742
8. Huo C, Zhang H, Guo J, Zhang H, Zhang P, Wang Y (2006) Synthesis and assembly with mesoporous silica of platinum (II) porphyrin complexes bearing carbazyl groups: luminescent and oxygen sensing properties. Chin Sci Bull 51:2327–2334
9. Wang Binbin, Zhang Liming, Li Bin, Li Yao, Shi Yuhua, Shi Tongshun (2014) Synthesis, characterization, and oxygen sensing properties of functionalized mesoporous silica SBA-15 and MCM-41 with a Pt(II)–porphyrin complex. Sens Actuators B Chem 190:93–100
10. Mao Li, Shi Tang, Fangzhong Shen, Meirong Liu, Feng Li, Ping Lu, Dan Lu, Muddasir Hanif, Yuguang Ma (2008) The Counter Anionic Size Effects on Electrochemical, Morphological, and Luminescence Properties of Electrochemically Deposited Luminescent Films. J Electrochem Soc 155:H 287-H291
11. Tang H, Tang H, Zhang Z, Yuan J, Cong C, Zhang K (2009) Synthesis, photoluminescent and electroluminescent properties of a novel europium(III) complex involving both hole- and electron-transporting functional groups. Synth Met 159:72–77
12. Zhao Z, Chen S, Deng C, Lam JWY, Chan CYK, Lu P, Wang Z, Hu B, Chen X, Kwok HS, Ma Y, Qjua H, Zhong B (2011) Construction of efficient solid emitters with conventional and AIE luminogens for blue organic light-emitting diodes. J Mater Chem 21:10949–10956
13. Tsuzuki T, Tokito S (2009) Highly efficient and stable organic light-emitting diode using 4,4′-bis(N-carbazolyl)-9,9′-spirobifluorene as a thermally stable host material. Phys Lett 94:33302
14. Domingues RA, Yoshida IVP, Atwars TD (2011) Synthesis, photophysical properties and thermal relaxation processes of carbazolyl-labeled polysiloxanes. J Photochem Photobiol A Chem 217:347–355
15. van Dijken A, Bastiaansen JJAM, Kiggen NMM, Langeveld BMW, Rothe C, Monkman A, Bach I, Stössel P, Brunner K (2004) Carbazole compounds as host materials for triplet emitters in organic light-emitting diodes: polymer hosts for high-efficiency light-emitting diodes. J Am Chem Soc 126:7718–7727
16. Cloutet E, Olivero C, Ades D, Castex MC, Siove A (2002) Synthesis and blue luminescence of a soluble newly designed carbazole main-chain polymer. Polymer 43:3489–3495

17. Bugatti V, Concilio S, Iannelli P, Piotto SP, Bellone S, Ferrara M, Neitzert HC, Rubino A, Sala DD, Vacca P (2006) Synthesis and characterization of new electroluminescent molecules containing carbazole and oxadiazole units. Synth Met 156:13–20
18. Rubino A, Sala DD, Vacca P (2006) Synthesis and characterization of new electroluminescent molecules containing carbazole and oxadiazole units. Synth Met 156:13–20
19. Concilio S, Bugatti V, Iannelli P, Piotto S (2010) Synthesis and characterization of new photoluminescent oxadiazole/carbazole-containing polymers. Int. J.Polymer Sci. (2010) 581056
20. Wong KT, Chen YM, Lin YT, Su HC, Wu CC (2005) Nonconjugated hybrid of carbazole and fluorene: a novel host material for highly efficient green and red phosphorescent OLEDs. Org Lett 24:5361–5364
21. Bruzga P, Grazulevicius JV, Kavaliunas R (1991) Cationic polymerization of 1,2-epoxy-6-(9-carbazolyl)-4-oxahexane. Eur. Polym. J. 27:707–711
22. Buika G, Grazulevicius JV (1993) Polymerization of 9-(2,3-epoxypropyl)carbazole with complexes of potassium compounds and 18-crown-6. Eur Polym J 29:1489–1493
23. Buika G, Grazulevicius JV, Stolarzewicz A, Grobelny Z (1995) Anionic polymerization of carbazolyl-substituted oxiranes initiated by potassium alkalide, potassium *tert*-butoxide and potassium hydride. Macromol Chem Phys 196:1287–1293
24. Grobelny Z, Stolarzewicz A, Morejko-Buż B, Buika G, Grazulevicius JV, Maercker A (2002) Study on the initiation step of 2-(9-carbazolyl)ethyl glycidyl ether polymerization by K^-, K^+ (15-crown-5)$_2$. Eur Polym J 38:2359–2363
25. Brown CA (1974) Potassium hydride, highly active new hydride reagent. Reactivity, applications, and techniques in organic and organometallic reactions. J Org Chem 39:3913–3918
26. Stolarzewicz A, Neugebauer D (1999) Influence of substituent on the polymerization of oxiranes by potassium hydride. Macromol Chem Phys 200:2467–2470
27. Stolarzewicz A, Neugebauer D, Grobelny J, Grobelny Z (1998) Polimeryzacja oksiranów w obecności wodorku potasu. Polimery 43:443–448
28. Spirin JU, Doroshenko N (1972) Study of the anionic polymerization of styrene oxide, Vysokomol. Soed Ser A 14:646–652
29. Grobelny Z, Matlengiewicz M, Jurek J, Michalak M, Kwapulińska D, Swinarew A, Schab E (2013) Balcerzak, The influence of macrocyclic ligands and water on propylene oxide polymerization initiated with anhydrous potassium hydroxide in tetrahydrofuran. Eur Polym J 49:3277–3288
30. Stolarzewicz A, Morejko B (2002) Buż, Z. Grobelny, D. Neugebauer, Analysis of the end groups of poly(methyl methacrylate). Macromol Symp 184:325–337