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Mendeleev Commun., 2021, **31**, 800–803

Mendeleev Communications

New benzodithiophene-pyrrolopyrroledione-thienopyrazine random terpolymers for organic photovoltaics

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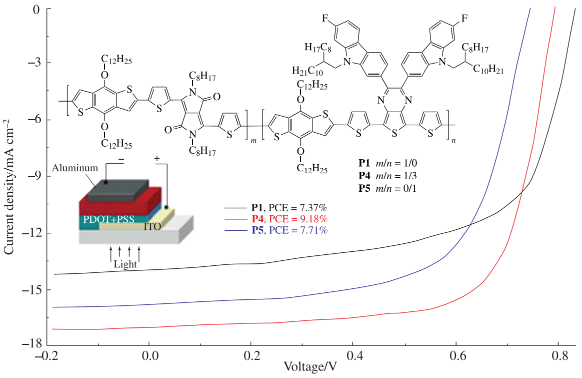
DOI: 10.1016/j.mencom.2021.11.010

New random ternary copolymers containing fragments of pyrrolo[3,4-*c*]pyrrole-1,4-dione, 2,3-bis[6-fluoro-9-(2-octyldodecyl)-9*H*-carbazol-3-yl]-3,3′-[5,7-di(thiophen-2-yl)-thieno[3,4-*b*]pyrazine as electron-withdrawing fragments and benzodithiophene as an electron-donor block have been synthesized. The best power conversion efficiency of 9.18% was achieved for the terpolymer with pyrrolopyrroledione/thienopyrazine ratio of 1 : 3. The introduction of the third thieno[3,4-*b*]pyrazine acceptor block into the structure of the 'parent' binary polymer can significantly adjust energy levels and the light absorption range of irregular copolymers, and can enhance photovoltaic properties due to improved absorption capacity and charge transfer.

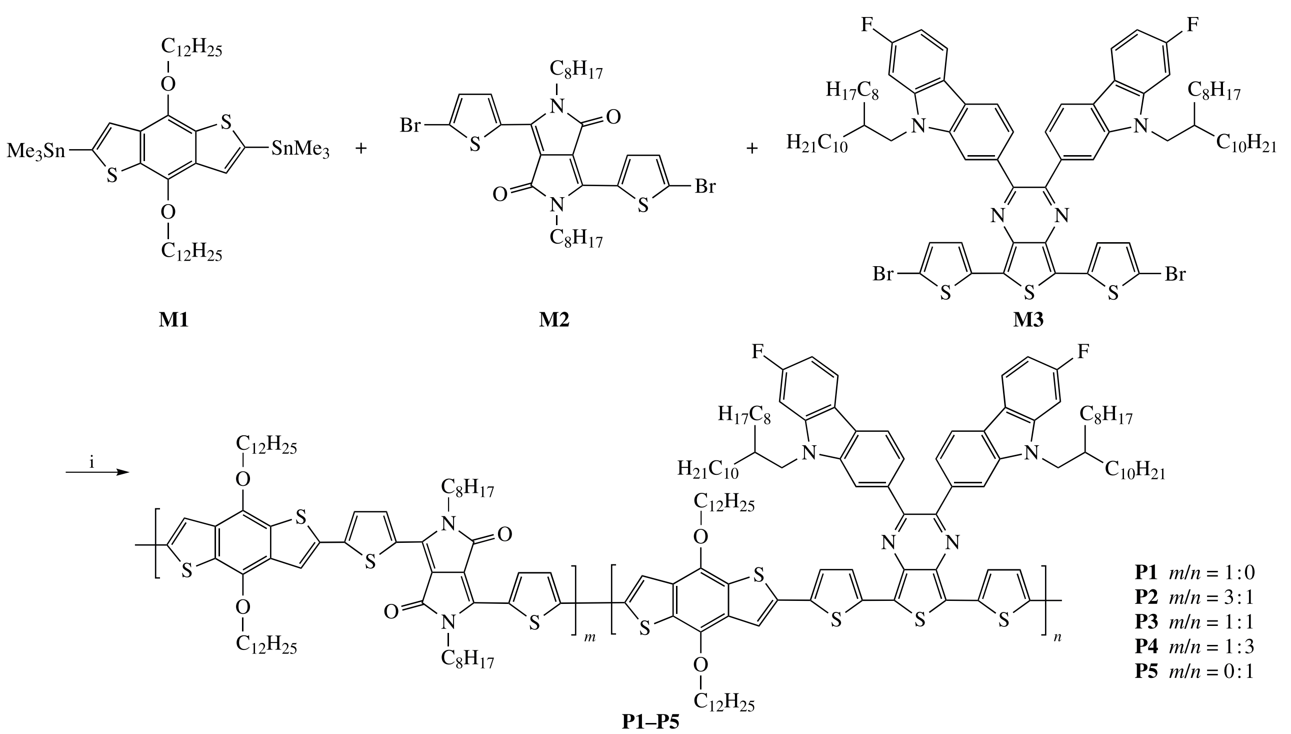


Keywords: polymer solar cells, random terpolymers, photovoltaic properties, pyrrolo[3,4-*c*]pyrroles, thieno[3,4-*b*]pyrazines.

Recently, polymer solar cells (PSCs) have attracted much attention as an environmentally friendly and renewable energy source due to unique advantages such as low cost, light weight, and the possibility to manufacture flexible large-area devices.[1] In this area, great progress has been made due to the development of new conjugated narrow-gap D–A copolymers.[2–4] However, as a rule, most narrow-gap polymers absorb beyond 600 nm due to strong intramolecular charge transfer between the donor and acceptor, and have weak absorption in significant part of visible region in 400–600 nm,[5–9] which limits the photocurrent. One of the strategies to overcome the aforementioned disadvantages is tandem solar cells.[10–12] However, the manufacture of tandem devices is an extremely complex process. PSCs based on ternary mixtures were also proposed to simplify the procedure for fabricating tandem solar cells, while maintaining the simplicity of fabricating single-layer cells.[13,14] However, the complexity of controlling the morphology in a ternary mixture leads to unfavorable interactions, a large number of charge traps and recombination centers, and, as a consequence, to a decrease in the photovoltaic characteristics of PSCs.[15] From this point of view, random ternary copolymers containing three different structural fragments in the main chain, one electron-donor and two different electron-acceptor blocks, seem promising.[16–19] The introduction of the third block in the polymer chain can provide a simultaneous improvement in physical properties such as absorption capacity, charge transfer, energy of electronic levels, as well as an increase in photovoltaic characteristics. In addition, the random ternary copolymers have increased solubility.[20] However, the number of successful examples of terpolymers with broad light absorption and high photovoltaic efficiency (PCE more than 10%) is relatively small; in addition, comparisons of irregular terpolymers of different compositions with their 'parent' binary D–A polymers have been rarely performed.[18]

Pyrrolo[3,4-*c*]pyrrole-1,4-dione ('diketo pyrrolopyrrole', DPP) and thieno[3,4-*b*]pyrazine (TPz) are among the most attractive acceptor blocks widely used in alternating D–A copolymers due to their high extinction coefficients, strong electron-acceptor ability, and molecular planarity.[21–24] In addition, benzo[1,2-*b*:4,5-*b*′]dithiophene (BDT) is one of the most widely used donor blocks for the development of D–A conjugated polymers due to its rigid and planar conjugated structure.[25,26] Meanwhile, PSCs based on D–A binary polymers DPP-BDT and TPz-BDT demonstrated a moderate efficiency of about 8.04 and 3.6%, respectively.[27,28] It should be noted that DPP-BDT binary copolymers exhibit intense absorption in the 600–900 nm range due to the strong influence of electron-acceptor lactam rings, but have weak absorption in the 300–600 nm range,[27] while the absorption bands of binary polymers BDT-TPz are in the range of 300–600 nm.[28] Therefore, a combination of electron-acceptor monomers such as DPP and TPz in the polymer chain can be an ideal pair to obtain a complementary broad absorption of polymers, which can contribute to an increase in the efficiency of PSCs based on them. Therefore, in this work, we have synthesized new ternary copolymers of the DPP-TPz-BDT type. We assumed that the optical and electrical properties of the obtained statistical terpolymers could be significantly improved, and the morphology of the mixture of active layers could be optimized due to the difference in the aggregate properties of TPz and DPP blocks, which would favor the efficiency of PSCs.

To study the influence of the compositional effects of electron-acceptor blocks **M2** and **M3** on the efficiency of PSCs,



Scheme 1 *Reagents and conditions*: i, $Pd(PPh_3)_4$, PhMe, reflux, 48 h.

three new irregular copolymers **P2**, **P3**, and **P4** with different molar ratios **M2/M3** were synthesized (**M2/M3** = 0.375 : 0.125 for **P2**, 0.25 : 0.25 for **P3**, and 0.125 : 0.375 for **P4**). The polymers were obtained by copolycondensation of an electron-donor distannyl monomer **M1** and two electron-acceptor dibromides **M2** and **M3** under the Stille reaction conditions (Scheme 1). To compare the properties, binary copolymers **P1** and **P5** were also obtained. Monomers **M1**,[29] **M2**,[30] and **M3**[31] were prepared according to the known methods.

The yields of polymers **P1–P5** amounted to 80–93%; their composition and structure were confirmed by elemental analysis and ^{1}H NMR spectroscopy. We noticed that it was not possible to determine ratios of DPP and TPz fragments in polymer chains from the ^{1}H NMR data because of low intensities and strong broadening of proton signals. Therefore, the only method to prove the composition in our case is elemental analysis, and these data are in a good agreement with the proposed structures of the polymers (see Online Supplementary Materials). The number averaged molecular weights (M_n) and polydispersity index (PDI) of copolymers **P1–P5** are in the range of 11.30–17.60 kDa and 1.52–2.21, respectively (Table 1). The copolymers are readily soluble in common organic solvents such as chloroform, chlorobenzene, *o*-dichlorobenzene, and THF, which makes it possible to obtain durable films for photovoltaic studies. All copolymers have high thermal stability, with a 5% polymer weight loss temperature (T_d) exceeding 330 °C, which is sufficient for photovoltaic applications (see Table 1 and Figure S1 of the Online Supplementary Materials).

Absorption spectra of copolymers **P1–P5** contain two absorption regions characteristic for D–A polymers (Figure 1, Table 2). The absorption band in the region of 300–500 nm refers to localized π–π* transitions, while the absorption peaks at 600–1000 nm refer to intramolecular charge transfer between the electron-donor BDT fragment and the electron-acceptor DPP or TPz units. It is noted that an increase in the content of the TPz block in the chain leads to a gradual increase in the absorption band at about 400 nm, while the absorption bands in the range of 600–1000 nm gradually decrease. On the contrary, when the TPz/DPP ratio is less than 0.25 : 0.25, the absorption in the long-wavelength region tends to stabilize, but sharply decreases in the short-wavelength region. In thin films, all copolymers exhibit broader absorption than solution due to stronger intermolecular aggregation. In addition, with an increase in the amount of DPP, the absorption shoulder around 700 nm gradually increases, which is associated with the strong aggregation of these DPP-based copolymers. The values of the optical band gap (E_g^{opt}) of polymers **P1–P5** calculated from the absorption edges of the films are 1.32, 1.30, 1.28, 1.27, and 1.25 eV, respectively (see Table 2). It can be seen that an increase in the amount of the TPz fragment in the polymers from **P1** to **P5** leads to a gradual decrease in the E_g^{opt} values, which favors an increase in the J_{sc} values. Thus, the results show that the inclusion of two electron-

Table 1 Polymerization yields, molecular weights, PDI and decomposition temperatures of terpolymers **P1–P5**.

Polymer (*m* : *n*)	Yield (%)	M_n/kDa^a	M_w/kDa^a	PDI (M_w/M_n)	T_d/°C^b
P1 (1 : 0)	93	11.3	20.6	1.82	358
P2 (3 : 1)	80	16.7	31.0	1.86	353
P3 (1 : 1)	85	12.3	18.6	1.52	347
P4 (1 : 3)	83	17.6	33.8	1.92	340
P5 (0 : 1)	89	12.4	27.4	2.21	333

^{a}Measured by GPC method in *o*-dichlorobenzene with polystyrene standards. ^{b}Temperature of 5% weight decreasing by the polymer sample.

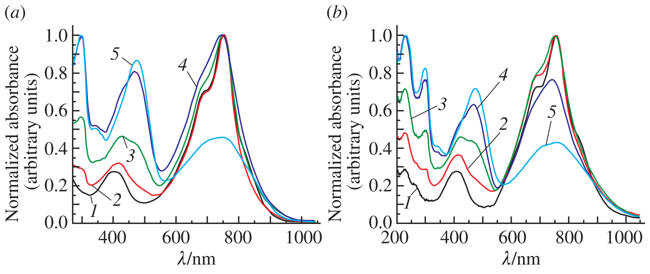


Figure 1 Normalized absorption spectra of the copolymers (*a*) in chloroform solutions and (*b*) in thin films: (*1*) **P1**, (*2*) **P2**, (*3*) **P3**, (*4*) **P4** and (*5*) **P5**.

Table 2 Optical and electrochemical properties of terpolymers **P1–P5**.

Polymer	$\lambda_{\max}$/nm		$E_{\rm HOMO}$/ eV^a	$E_{\rm LUMO}$/ eV^a	$E_g^{\rm ech}$/ eV^b	$E_g^{\rm opt}$/ eV^c
	$CHCl_3$	film				
P1	405, 753	410, 758	–5.23	–3.60	1.63	1.32
P2	422, 753	415, 760	–5.22	–3.61	1.61	1.30
P3	297, 430, 749	302, 430, 760	–5.21	–3.60	1.60	1.28
P4	297, 470, 744	300, 471, 743	–5.16	–3.59	1.57	1.27
P5	297, 473, 750	298, 475, 763	–5.14	–3.61	1.53	1.25

[a] HOMO/LUMO energy levels were calculated from the onsets of electrochemical oxidation ($E_{\rm ox}^{\rm ons}$) and reduction ($E_{\rm red}^{\rm ons}$) potentials of the polymer films, according to the equations $E_{\rm HOMO} = -(E_{\rm ox}^{\rm ons} + 4.44)$ (eV), $E_{\rm LUMO} = -(E_{\rm red}^{\rm ons} + 4.44)$ (eV); [b] $E_g^{\rm ech} = E_{\rm LUMO} - E_{\rm HOMO}$; [c] $E_g^{\rm opt} = 1240/\lambda_{\rm abs\ edge\ film}$.

acceptor units in the main chain of a macromolecule with controlled molar ratios (TPz/DPP) is an effective strategy for expanding the absorption range and directionally changing the band gap of terpolymers.

The energies of the HOMO/LUMO levels of copolymers **P1–P5** determined by cyclic voltammetry are –5.23/–3.60, –5.22/–3.61, –5.21/–3.60, –5.16/–3.59 and –5.14/–3.61 eV, respectively (see Table 2 and Figure S2). All polymers exhibit low energies of HOMO levels, which favors high open-circuit voltage ($V_{\rm oc}$) of PSCs based on them. With an increase in the content of DPP fragments in the main chain of the macromolecule in copolymers **P1–P5**, the energy of the HOMO level gradually decreases, while the energy of the LUMO remains practically constant (~ –3.6 eV), which leads to a decrease in the band gap and favors an increase in the short-circuit current ($J_{\rm sc}$) of the photocells. The energy difference $\Delta E_{\rm HOMO-LUMO}$ of the polymers and [6,6]-phenyl C_{71} butyric acid methyl ester ($PC_{71}BM$) ($E_{\rm LUMO} = -4.2$ eV) is in the range of 0.61–0.59 eV and exceeds 0.3 eV, which is sufficient for efficient separation of excitons into free charge carriers. The results obtained show that the HOMO energies of random terpolymers can be finely tuned by adjusting the ratio of DPP/TPz acceptor blocks in the main chains of macromolecules; thus it is possible to achieve an improvement in the voltage $V_{\rm oc}$ of the PSCs. The $E_{\rm g}^{\rm ech}$ values determined electrochemically vary in the range of 1.63–1.53 eV, which is higher than the optical band gap ($E_{\rm g}^{\rm opt}$) of the copolymers. This discrepancy is apparently associated with the energy barrier between the polymer film and the electrode surface.[31]

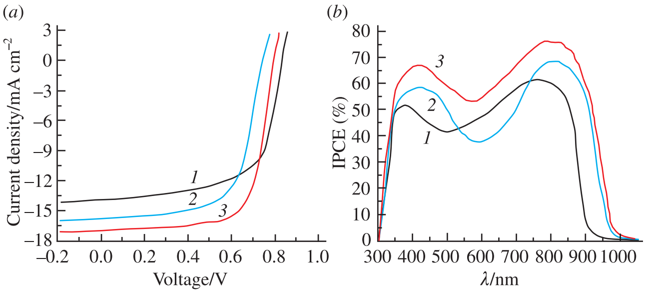


Figure 2 (*a*) *J–V* plots and (*b*) IPCE spectra of the optimized active layers based on the copolymers: (*1*) **P1**, (*2*) **P5** and (*3*) **P4**.

Table 3 Photovoltaic characteristics of optimized PSCs based on **P1–P5**: $PC_{71}BM$ active layers.[a]

Polymer	$J_{\rm sc}$/mA cm^{-2}	$V_{\rm os}$/V	FF (%)	PCE (%)
P1	13.88 (±0.12)	0.83 (±0.020)	64 (±0.005)	7.37 (±0.18)
P2	14.45 (±0.14)	0.83 (±0.020)	66 (±0.006)	7.91 (±0.21)
P3	16.23 (±0.21)	0.81 (±0.020)	66 (±0.007)	8.68 (±0.25)
P4	16.84 (±0.25)	0.79 (±0.012)	69 (±0.007)	9.18 (±0.19)
P5	15.63 (±0.16)	0.76 (±0.011)	65 (±0.004)	7.72 (±0.17)

[a] *J–V* characteristics and IPCE spectra were measured under ambient conditions; the effective area of the devices are 16 mm^2; the active layer films were dried at 40 °C without any annealing; the characteristics of the devices were stable for 70 h period of time.

Bulk heterojunction polymer solar cells based on the synthesized copolymers **P1–P5** as donors and $PC_{71}BM$ as an acceptor, with the configuration of ITO/PEDOT : PSS/active layer/PFN/Al were fabricated. The PSCs were optimized by adjusting the copolymer/$PC_{71}BM$ weight ratios, the thickness of the photoactive layers, and the concentration of solvent additive. It was found that the weight ratio D/A = 1 : 2 and the addition of 3% DIO to the basic solvent (chloroform) is optimal. The devices were fabricated under ambient conditions. Figure 2(*a*) shows the graphs of the dependence of the current density on the voltage (*J–V*) when the solar cells are illuminated with the AM1.5G light (100 mW cm^{-2}), and the corresponding photovoltaic parameters are presented in Table 3. All the measurements were carried out in air. It can be seen that for the PSCs based on **P1** and **P2**, almost the same $V_{\rm os}$ values were observed, while $V_{\rm os}$ is lower for the **P5**-based PSCs, which is consistent with the relative position of the HOMO levels of these statistical copolymers, since the $V_{\rm os}$ value is proportional to the difference between the $E_{\rm LUMO}$ and $E_{\rm HOMO}$ of the acceptor and donor materials. With an increase in the content of the TPz fragment in terpolymers, the $J_{\rm sc}$ value gradually increases, reaching the highest value for the **P4** : $PC_{71}BM$ mixture, which is apparently associated with the broader absorption spectra of **P4** in comparison with other polymers [see Figure 1(*b*)]. The device based on **P1** : $PC_{71}BM$ showed an efficiency of 7.37%; among all of the copolymers, PSC based on **P4** : $PC_{71}BM$ demonstrated the highest efficiency of 9.18% with $V_{\rm oc}$ of 0.79 eV, $J_{\rm sc}$ of 16.84 mA cm^{-2} and a fill factor (FF) of 69% (although $V_{\rm os}$ is slightly lower than in the case of PSCs based on **P1–P3**), which is explained by the higher values of $J_{\rm sc}$ and FF in comparison with PSCs based on other copolymers. The external quantum efficiency (IPCE) plots of optimized devices based on polymers **P1**, **P4** and **P5** are shown in Figure 2(*b*). All three devices showed a broad spectral response in the 300–900 nm wavelength range with an IPCE maximum of over 70%. As shown in Figure 2(*b*), the IPCE values for the **P4** : $PC_{71}BM$-based PSCs are higher than for the other two devices; the IPCE spectrum for **P4** : $PC_{71}BM$ is the broadest and is very similar to the absorption spectrum of the ternary copolymer. The $J_{\rm sc}$ values obtained for devices based on **P1**, **P4**, and **P5** by integrating the IPCE spectra are 13.75, 16.73, and 12.38 mA cm^{-2}, respectively, which are consistent with the $J_{\rm sc}$ values obtained from the *J–V* characteristics.

In conclusion, a series of new random terpolymers **P1** (DPP/TPz = 1 : 0), **P2** (DPP/TPz = 3 : 1), **P3** (DPP/TPz = 1 : 1), **P4** (DPP/TPz = 1 : 3), **P5** (DPP/TPz = 0 : 1) based on benzo[1,2-*b*:4,5-*b*]dithiophene (BDT) as an electron-donor unit and two electron-acceptor units (DPP and TPz) have been designed and synthesized. Compared to binary polymers (**P1** and **P5**), terpolymers exhibit broader absorption spectra covering the range from 300 to 1000 nm. It is of note that an increase in the content of the TPz block in the main chain leads to a gradual increase in the absorption band at about 400 nm, while the absorption bands in the range of 600–1000 nm gradually decrease. On the contrary, when the TPz/DPP ratio is less than 0.5 : 0.5, the absorption in the long-wavelength region tends to stabilize, but sharply decreases in the short-wavelength region. With an increase in the content of DPP fragments in the main chain of the macromolecule in ternary copolymers **P1–P5**, the HOMO energy gradually decreases, while the LUMO energy remains practically constant (~ –3.6 eV), which leads to a decrease in the band gap and favors an increase in $J_{\rm sc}$. Among all terpolymers, **P4** showed the best efficiency with the PCE of

9.18% in **P4** : $PC_{71}BM$-based PCSs. The results indicate that the inclusion of two electron-acceptor units into the main chain of a macromolecule with controlled molar ratios (TPz/DPP) is an effective strategy for expanding the absorption range and regulation of the HOMO energy levels of statistical copolymers, and, as a consequence, increasing the efficiency of PSCs.

NMR spectroscopy studies and elemental analysis were supported by the Ministry of Science and Higher Education of the Russian Federation and were performed using research equipment of the Center of Investigation of Molecular Structure at the A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences.

The reported study was funded by RFBR according to the research project nos. 18-53-80066, 18-29-23004 and 21-53-53037.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2021.11.010.

References

1 C. Liu, K. Wang, X. Gong and A. J. Heeger, *Chem. Soc. Rev.*, 2016, **45**, 4825.

2 Y. Gao, M. Liu, Y. Zhang, Z. Liu, Y. Yang and L. Zhao, *Polymers*, 2017, **9**, 39.

3 M. C. Scharber and N. S. Sariciftci, *Adv. Mater. Technol.*, 2021, **6**, 2000857.

4 C. Cui and Y. Li, *Energy Environ. Sci.*, 2019, **12**, 3225.

5 A. Tang, F. Chen, B. Xiao, J. Yang, J. Li, X. Wang and E. Zhou, *Front. Chem.*, 2018, **6**, 147.

6 G. Zhang, J. Yuan, P. Li, J. Ma, H. Lu, L. Qiu and W. Ma, *Polym. Chem.*, 2013, **4**, 3390.

7 L. Cartwright, T. J. Neal, N. J. Rutland and A. Iraqi, *Polym. Adv. Technol.*, 2016, **27**, 525.

8 Y. Wang, T. Hasegawa, H. Matsumoto and T. Michinobu, *Angew. Chem., Int. Ed.*, 2019, **58**, 11893.

9 Q. Liu, Y. Jiang, K. Jin, J. Qin, J. Xu, W. Li, J. Xiong, J. Liu, Z. Xiao, K. Sun, S. Yang, X. Zhang and L. Ding, *Sci. Bull.*, 2020, **65**, 272.

10 L. Dou, J. You, J. Yang, C. C. Chen, Y. He, S. Murase, T. Moriarty, K. Emery, G. Li and Y. Yang, *Nat. Photonics*, 2012, **6**, 180.

11 Z. Zheng, S. Zhang, M. Zhang, K. Zhao, L. Ye, Y. Chen, B. Yang and J. Hou, *Adv. Mater.*, 2015, **27**, 1189.

12 L. Meng, Y. Zhang, X. Wan, C. Li, X. Zhang, Y. Wang, X. Ke, Z. Xiao, L. Ding, R. Xia, H.-L. Yip, Y. Cao and Y. Chen, *Science*, 2018, **361**, 1094.

13 J. Zhang, Y. Zhang, J. Fang, K. Lu, Z. Wang, W. Ma and Z. Wei, *J. Am. Chem. Soc.*, 2015, **137**, 8176.

14 A. D. Fenta, C.-F. Lu, A. T. Gidey and C.-T. Chen, *ACS Appl. Energy Mater.*, 2021, **4**, 5274.

15 P. P. Khlyabich, B. Burkhart and B. C. Thompson, *J. Am. Chem. Soc.*, 2012, **134**, 9074.

16 T. E. Kang, K.-H. Kim and B. J. Kim, *J. Mater. Chem. A*, 2014, **2**, 15252.

17 Y. Liu, F. Wu, B. Zhao and P. Shen, *Eur. Polym. J.*, 2016, **74**, 180.

18 X. Gao, Y. Wu, Y. Tao and W. Huang, *Chin. J. Chem.*, 2020, **38**, 601.

19 P. M. Kuznetsov, I. E. Kuznetsov, I. V. Klimovich, P. A. Troshin and A. V. Akkuratov, *Mendeleev Commun.*, 2021, **31**, 30.

20 B. Burkhart, P. P. Khlyabich and B. C. Thompson, *ACS Macro Lett.*, 2012, **1**, 660.

21 C. B. Nielsen, M. Turbiez and I. McCulloch, *Adv. Mater.*, 2013, **25**, 1859.

22 Y. Li, P. Sonar, L. Murphy and W. Hong, *Energy Environ. Sci.*, 2013, **6**, 1684.

23 R. Mondal, S. Kob and Z. Bao, *J. Mater. Chem.*, 2010, **20**, 10568.

24 S. C. Rasmussen, R. L. Schwiderski and M. E. Mulholland, *Chem. Commun.*, 2011, **47**, 11394.

25 L. Huo and J. Hou, *Polym. Chem.*, 2011, **2**, 2453.

26 H. Yao, L. Ye, H. Zhang, S. Li, S. Zhang and J. Hou, *Chem. Rev.*, 2016, **116**, 7397.

27 L. Ye, X. Jiao, S. Zhang, H. Yao, Y. Qin, H. Ade and J. Hou, *Adv. Energy Mater.*, 2016, **7**, 1601138.

28 T. T. T. Bui, C. E. Song, S. Park, J.-C. Lee, S. K. Lee, S.-J. Moon and W. S. Shin, *Sci. Adv. Mater.*, 2016, **8**, 657.

29 J. Hou, M.-H. Park, S. Zhang, Y. Yao, L.-M. Chen, J.-H. Li and Y. Yang, *Macromolecules*, 2008, **41**, 6012.

30 G.-Y. Chen, C.-M. Chiang, D. Kekuda, S.-C. Lan, C.-W. Chu and K.-H. Wei, *J. Polym. Sci., Part A: Polym. Chem.*, 2010, **48**, 1669.

31 M. L. Keshtov, S. A. Kuklin, I. O. Konstantinov, A. S. Peregudov, A. V. Muranov and A. R. Khokhlov, *Dokl. Chem.*, 2017, **472**, 25 (*Dokl. Akad. Nauk*, 2017, **472**, 670).

Received: 16th April 2021; Com. 21/6528