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Synthesis of siloxane analogue of polyethylene terephthalate

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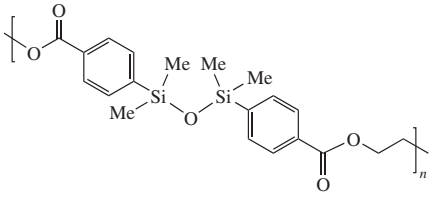
New large-capacity polyethylene terephthalate siloxane analogue was obtained by $Zn(OAc)_2$-promoted polycondensation of 1,3-bis[*p*-(methoxycarbonyl)phenyl]disiloxane with ethylene glycol at 200 °°°C. The thermal and thermooxidative stabilities of the polymer were evaluated.



The creation of new polymeric materials is an important direction for modern materials science. Scientific tasks in search for new high-molecular compounds possessing improved properties include the synthesis of fundamentally new monomers, development of experimental procedures of assembling of macromolecules, and transformations of polymers. One more general task is the modification of monomers, which would lead to change in the structure of the main chain. We were aimed at obtaining a siloxane analogue of such a large-capacity polymer as polyethylene terephthalate (PET). It is known that copolymers with organic and siloxane units exhibit new valuable properties, combining the advantages of both fragments.[1–6] The PET-based materials are used in the production of fibers, food films and plastics for construction, medicine, electronics, *etc*.[7]

Polyethylene terephthalate possesses high strength and wear resistance, as well as high electrical resistivity.[7] However, in some cases the processing of PET products is seriously hampered by their hygroscopicity and low solubility in organic solvents and water, as well as the tendency to crystallization, in addition to the relatively low thermal stability and high glass transition temperature. It was assumed that the introduction of a hydrophobic and flexible siloxane fragment into the structure of PET would somewhat improve the properties.

Herein, we have suggested a siloxane analogue, 1,3-bis(*p*-carboxyphenyl)disiloxane **1** (Scheme 1), as a substitute for terephthalic acid.[8–10]

By analogy with the classical method of obtaining PET, in the first stage, 1,3-bis[*p*-(methoxycarbonyl)phenyl]disiloxane **2** was synthesized by reacting diacid **1** with methanol in the presence of dicyclohexylcarbodiimide (DCC) and DMAP in 70% yield.

Sila-PET polymer **3** was synthesized in two stages. First, dimethyl ester **2** was transesterified with ethylene glycol in the presence of 5 mol% zinc acetate catalyst at 200 °C. Next, vacuum transcondensation was performed *in situ* at 230 °C and residual pressure of 1 mbar to result in 95% yield of polymer **3**.

Compound **2** was characterized by ^{1}H, ^{13}C, ^{29}Si NMR and IR spectroscopy as well as HRMS data. For polymer **3**, ^{1}H, ^{13}C, ^{29}Si NMR, IR and GPC (Figure 1) experiments were performed.[†]

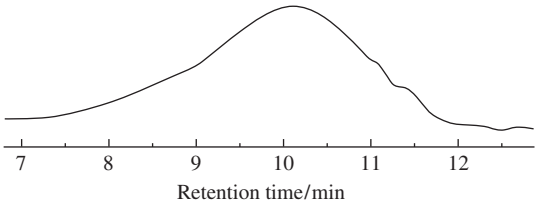
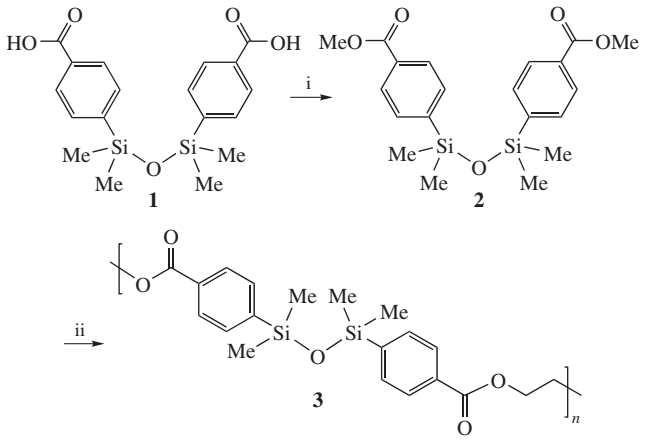


Figure 1 GPC curve of polymer **3** (M_n = 3 kDa, M_w = 8.7 kDa, PDI = 2.9).



Scheme 1 *Reagents and conditions*: i, MeOH, DCC, DMAP, THF, 25 °C; ii, $HO(CH_2)_2OH$, $Zn(OAc)_2$ (5 mol%), 200 °C, then evacuation at 1 mbar/230 °C.

[†] All the starting materials were purchased from Acros and Sigma Aldrich. Gel permeation chromatography (GPC) was performed on a Shimadzu instrument, RID-20A refractometer as a detector, Phenogel 5u 10000A column (300 × 7.8 mm), polystyrene as a strandard, THF as an eluent, 40 °C, eluent flow of 1 ml s^{-1}. High resolution mass spectra (HRMS) were recorded on a Bruker Daltonics micrOTOF-Q II instrument using electrospray ionization (ESI). IR spectra (films for liquids or pellets for solids) were obtained on a Bruker Tensor 37 FTIR spectrometer. ^{1}H, ^{13}C, ^{29}Si NMR spectra were recorded using a Bruker Avance 400 NMR spectrometer in $CDCl_3$, chemical shifts were referenced to residual chloroform (7.26 ppm, ^{1}H). Thermogravimetric analysis (TGA) was performed using Mettler TG50 thermo-balance in the range from 50 to 700 °C at a heating rate of 10 K min^{-1} in nitrogen or synthetic air (80% nitrogen and 20% oxygen) atmosphere.

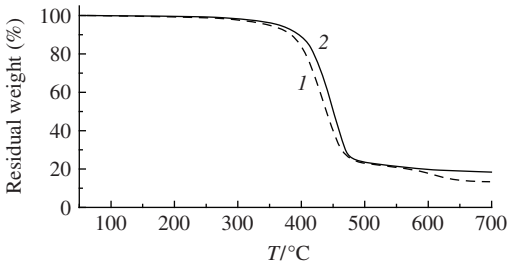


Figure 2 TGA curves of polymer **3** in (*1*) air and (*2*) nitrogen.

The obtained Sila-PET demonstrates high thermal and thermal-oxidative stability and rather good solubility in low-polar and polar aprotic solvents (THF, toluene, acetone, chloroform, dichloromethane, benzene, and ethyl acetate). Its contact wetting angle was 80°, which was 10° higher than that of PET (70°).

The thermogravimetric data for polymer **3** are shown in Figure 2. Its temperatures of beginning of intense destruction are 410 °C in the inert atmosphere and 390 °C in air, which is in a good agreement with those for commercial PET.[11] At the same time, the temperature of beginning of destruction in air (the temperature of 5% weight loss, $T_d^{5\%}$) of sample **3** is 350 °C, which is just 5 °C lower than the value of this parameter for commercial PET. However, the $T_d^{5\%}$ of polymer **3** in nitrogen is 365 °C *vs*. 405 °C typical of PET.[11] Probably this discrepancy is due to the presence of some low molecular weight fraction in the obtained sample **3**.

Further investigations will be focused on studies of the physicochemical properties of the synthesized polymer and the preparation of high-molecular polymers in order to analyze the feasibility of further use in coatings, fibers, membranes, *etc*.

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*1,3-Bis[*p*-(methoxycarbonyl)phenyl]disiloxane* **2**. Diacid **1** (0.97 g, 2.58 mmol), DCC (1.07 g, 5.16 mmol), DMAP (0.02 g, 0.16 mmol) and THF (25 ml) were stirred in a 50 ml round bottomed flask at 0 °C for 6 h. Then MeOH (0.25 g, 7.70 mmol) was added, and the mixture was stirred for more 12 h. The solvent was evaporated (340–360 mbar, 40 °C) and the residue was dissolved in CH_2Cl_2 (25 ml) and filtered through 5 cm layer of SiO_2, then SiO_2 was additionally washed with 250 ml of CH_2Cl_2. The filtrate was concentrated (600 mbar, 40 °C) to leave diester **2** as a white solid in 70% yield (0.73 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.37 (s, 12H), 3.94 (s, 6H), 7.62 (d, 4H), 8.00 (d, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 0.66, 52.07, 128.58, 130.84, 132.93, 145.47, 167.17. ^{29}Si NMR (80 MHz, $CDCl_3$) δ: –0.67. IR (ν/cm^{-1}): 2955, 1723, 1441, 1282, 1259, 1099 (Si–O–Si), 1059, 842, 794, 758. HRMS (ESI), *m*/*z*: 420.17 (calc. for $C_{20}H_{26}O_5Si_2$ $[M+NH_4]^+$, *m*/*z*: 420.17).

Synthesis of polymer **3**. Diester **2** (200 mg, 0.497 mmol), ethylene glycol (67 mg, 1.093 mmol), $Zn(OAc)_2 \cdot 2H_2O$ (5 mg, 0.02 mmol) were stirred in Schott culture tubes (160×16 mm) at 200 °C for 4 h. Then the mixture was additionally kept in Kugelrohr at 200–240 °C for 4 h at 1 mbar. The residue was analyzed by GPC (eluent, THF; standard, polystyrene; 500 kDa). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.36, 3.94, 4.69, 7.61, 8.03. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 0.58, 0.69, 52.08, 62.76, 128.60, 128.66, 128.74, 130.51, 132.97, 145.81, 166.42. ^{29}Si NMR (80 MHz, $CDCl_3$) δ: –0.64 (br.). IR (ν/cm^{-1}): 2958, 1725, 1389, 1286, 1260, 1092 (Si–O–Si), 1019, 832, 794, 757, 453.

References

1 D. E. Hagaman, S. Leist, J. Zhou and H.-F. Ji, *ACS Appl. Mater. Interfaces*, 2018, **10**, 27308.
2 A. R. Ashraf, Z. Akhter, V. McKee and M. Siddiq, *eXPRESS Polym. Lett*., 2015, **9**, 1001.
3 Y. Zhang, C. Dai, S. Zhou and B. Liu, *Chem. Commun*., 2018, **54**, 10092.
4 H. Gojzewski, J. Obszarska, A. Harlay, M. A. Hempenius and G. J. Vancso, *Polymer*, 2018, **150**, 289.
5 F. V. Drozdov, G. V. Cherkaev and A. M. Muzafarov, *Mendeleev Commun*., 2017, **27**, 570.
6 A. A. Pakhomov, V. B. Mironiuk, Yu. N. Kononevich, A. A. Korlyukov, A. D. Volodin, T. A. Pryakhina, V. I. Martynov and A. M. Muzafarov, *Mendeleev Commun*., 2017, **27**, 363.
7 *NPCS Board of Consultants & Engineers, Disposable Products Manufacturing Handbook*, NIIR Project Consultancy Services, Delhi, 2014, ch. 6, p. 56.
8 I. K. Goncharova, A. V. Arzumanyan, S. A. Milenin and A. M. Muzafarov, *J. Organomet. Chem*., 2018, **862**, 28.
9 I. K. Goncharova, K. P. Silaeva, A. V. Arzumanyan, A. A. Anisimov, S. A. Milenin, R. A. Novikov, P. N. Solyev, Y. V. Tkachev, A. D. Volodin, A. A. Korlyukov and A. M. Muzafarov, *J. Am. Chem. Soc*., 2019, **141**, 2143.
10 A. V. Arzumanyan, I. K. Goncharova, R. A. Novikov, S. A. Milenin, K. L. Boldyrev, P. N. Solyev, Y. V. Tkachev, A. D. Volodin, A. F. Smol'yakov, A. A. Korlyukov and A. M. Muzafarov, *Green Chem*., 2018, **20**, 1467.
11 S. A. Jabarin and E. A. Lofgren, *Polym. Eng. Sci*., 1984, **24**, 1056.

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