



Cite this: *Chem. Commun.*, 2023, 59, 11228

Received 23rd June 2023,
Accepted 31st July 2023

DOI: 10.1039/d3cc03029f

rsc.li/chemcomm

Catalyst-free depolymerization of polycaprolactone to silylated monoesters and iodide derivatives using iodosilanes†

Xin Liu, Marie Kobylarski, Jean-Claude Berthet* and Thibault Cantat *

The homogeneous depolymerization of polycaprolactone (PCL) with excess iodotrimethylsilane (Me_3SiI) proceeds without catalysts and selectively afforded $\text{I}(\text{CH}_2)_5\text{CO}_2\text{SiMe}_3$ or a mixture of $\text{I}(\text{CH}_2)_5\text{CO}_2\text{SiMe}_3$ and $\text{I}(\text{CH}_2)_5\text{CO}_2\text{I}$ depending on the solvent (CH_2Cl_2 , MeCN). The latter mixture can undergo methanolysis or hydrolysis into the valuable ester $\text{I}(\text{CH}_2)_5\text{CO}_2\text{Me}$ or the acid $\text{I}(\text{CH}_2)_5\text{CO}_2\text{H}$. In contrast, SiH_2I_2 depolymerized PCL into the fully deoxygenated species $\text{I}(\text{CH}_2)_6\text{I}$ and *n*-hexane.

Plastics have many advantages over traditional materials (glass, wood, etc.). They are cheap, durable, easy to shape and have adjustable properties. They have strongly contributed to the post war economic rise by encouraging mass consumption with the abundance of cheap and disposable objects. The production of plastics has grown from 15 Mt in the mid-60's to ~460 Mt in 2020 and is projected to double in the next 20 years.^{1,2} However, plastics also pose a serious environmental problem. About half of the plastics are used only once and then thrown away, generating 350 Mt/year of plastic waste.^{3,4} Most of this waste is not recycled and ends up in landfills or oceans. Out of the 9.2 billion tons of plastic produced since the beginning, less than 8% would have been recycled and around 13 Mt of waste are released into the oceans every year.⁵

These frightening figures underline the need to move towards a circular economy and to more sober plastic consumption. In addition to the reuse and repair of objects, the plastic industry will have to significantly reduce its negative externalities and recover the carbonaceous matter from waste. In this context, chemical recycling that is the depolymerization of plastic materials into monomers or valuable compounds useful for the chemical industry is appealing and has emerged as a long-term sustainable strategy. At present, less than 1% of plastics are chemically recycled in Europe.⁶ The few existing

industrial processes to depolymerize plastics are based essentially on catalytic solvolysis processes (hydrolysis, aminolysis or transesterification reactions), that give back the corresponding monomers, or thermal treatments (gasification, pyrolysis) to produce syngases and hydrocarbon fractions.⁷ These processes are technologically advanced but their future also depends on their economic viability.

Recent fundamental advances in that field concern the reductive depolymerization of oxygenated or nitrogenated polymers using homogeneous catalysts in presence of hydride source (H_2 or SiH/BH reductants).^{8–13} In particular, building on the previous works on the carbon–oxygen bond cleavage by hydrosilanes in homogeneous catalysis, we and others have used organosilicon hydrides (R_3SiH) and various $\text{Ir}(\text{III})$, $\text{Mo}(\text{VI})$, $\text{Zr}(\text{IV})$ or $\text{Zn}(\text{II})$ or boron catalysts, to break down oxygenated plastics (polyesters, polyethers, polycarbonates) into valuable alcohols and alkanes.^{8,14,15} Silyl ethers and even hydrocarbons compounds derived from the true monomers were formed selectively by adjusting the reaction parameters (temperature, type and amount of the reductant, solvent). However, chemical depolymerization of oxygenated polymers with other silicon reagents, especially those with reactive Si–X bonds such as halides ($\text{X} = \text{I}$, Cl , Br), has not been explored to produce functionalized monomer molecules. We hypothesized that the iodosilane reagents with the weakest Si–X bond ($\text{BDE}(\text{Si–I}) \approx 70\text{--}80 \text{ kcal mol}^{-1}$),^{16,17} could favor the formation of a high-energy Si–O bond ($90\text{--}110 \text{ kcal mol}^{-1}$), without the need for a catalytic activation.¹⁸

Organosilicon reagents have been studied in organic chemistry since the end of the 70's. Many studies report the capabilities of the reactive Me_3SiI (Me_3SiCl and Me_3SiBr proved inefficient), SiH_2I_2 or of combined reagents ($\text{Me}_3\text{SiCl}\text{--NaI}$, $\text{SiH}_2\text{I}_2\text{--I}_2\text{...}$) to cleave carbon–oxygen bonds in ethers, esters, carbamates, ketals and alcohols, and to deoxygenate sulfoxides ($\text{R}_2\text{S=O}$).^{19–24} Reactions of the monoesters $\text{RCO}_2\text{R}'$ with different halosilanes led to the silylated esters and then the acyl iodide as shown in Scheme 1.

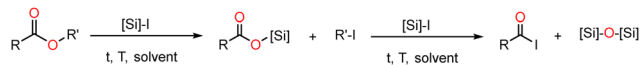
These studies prompted us to explore the potential of two iodosilanes (Me_3SiI and SiH_2I_2) in the depolymerization of

NIMBE, CEA Paris-Saclay, Gif-sur-Yvette Cedex 91191, France.

E-mail: thibault.cantat@cea.fr, jean-claude.berthet@cea.fr

† Electronic supplementary information (ESI) available. See DOI: <https://doi.org/10.1039/d3cc03029f>





Scheme 1 Reaction of monoesters with iodosilanes.

polyesters, with the aim to produce silylated and iodo functionalized monomers of interest in organic and materials chemistry. In this communication, we focused on the depolymerization of polycaprolactone (PCL), as a model synthetic polyester. We report that under refluxing conditions and without any catalyst, Me₃SiI and SiH₂I₂ are relevant reagents to cleanly depolymerize polycaprolactone (PCL) into value added silyl ester monomers and/or reactive iodide derivatives. Unexpectedly, we observed for the first time the ability of SiH₂I₂ to promote both iodide and hydride transfers to cleave C–O bonds providing diiodohexane and *n*-hexane.

Polycaprolactone (PCL) is a biodegradable synthetic polyester that found applications in various industrial fields such as coatings, adhesives, sealants and polyurethane elastomers.^{25,26} It is also broadly applied in biomedical applications, specifically in tissue engineering, sutures, drug delivery, *etc.* It is produced industrially mainly by ring-opening polymerization of ϵ -caprolactone and polycondensation of carboxylic acid methods on million tons/year with a market size valued at 415 million€ and projected to reach *ca.* 1 billion€ within 2030.²⁷

Our attempts to depolymerize polyesters with Me₃SiI were carried out with commercial pellets of PCL. Main results are reported in Table 1. Addition of a slight excess of Me₃SiI (1.2 equiv.) to pellets of PCL in CD₂Cl₂ showed only 1% of conversion after 20 h at 25 °C (Table 1, entry 1). At 50 °C, the conversion reached 24% after 5 h, with clean formation of I(CH₂)₅CO₂SiMe₃ (1) (Table 1, entry 2). This yield is doubled when warming at 100 °C (46% after 5 h) (Table 1, entry 3).

Table 1 Depolymerization of PCL with Me₃SiI- Optimization of the reaction conditions^a

Entry	x (equiv.)	Solvent	T (°C)	t (h)	Yield in 1 (%) ^b	Yield in 2 (%) ^b
1	1.2	CD ₂ Cl ₂	25	20	Traces	0
2	1.2	CD ₂ Cl ₂	50	5	24	0
3	1.2	CD ₂ Cl ₂	100	5	46	0
4	1.2	CD ₂ Cl ₂	130	2	78	0
5	1.2	CD ₂ Cl ₂	150	2	88	0
6	2	CD ₂ Cl ₂	100	5	74	0
				40	> 99	Traces
7	2	CH ₂ Cl ₂	100	15	95 ^c	—
8	2	CD ₃ CN	100	5	90	10
9	2	CD ₃ CN	130	2	83	17
10 ^d	2	CD ₃ CN	150	2	68	32
11 ^d	6	CD ₃ CN	150	16	23	74
12 ^e	3	CD ₂ Cl ₂	150	10	23	77

^a Conditions: PCL (0.28 mmol with respect to the monomer unit), solvent (0.4 mL). ^b Yields in 1 and 2 determined by integration of their ¹H NMR signals vs. those of dodecane (standard). ^c Isolated yield containing 2% of 2. ^d Approximate ratio by ¹H NMR due to H/D exchange (see ESI). ^e Addition of 1 equiv. I₂.

Increasing the temperature to 130 °C and 150 °C boosted the kinetic of depolymerization: after only 2 h, 78% and 88% of **1** were respectively obtained (Table 1, entries 4–5). The formation of **1** demonstrates, for the first time, the ability of iodosilanes to promote the depolymerization of polyesters under metal-free conditions. In presence of excess Me₃SiI (2 equiv.), a CD₂Cl₂ solution of PCL heated at 100 °C gave **1** in a better yield (74% after 5 h) (Table 1, entry 6) than with 1.2 equiv. Me₃SiI (Table 1, entry 3) and the formation of **1** is almost quantitative (> 99%) after prolonged heating (40 h at 100 °C) with no side-products (Table 1, entry 6). A scale-up using this procedure (15 h at 100 °C in CH₂Cl₂; 2 equiv. Me₃SiI) afforded **1** in 95% yield (96% purity) as a pale yellow oil after evaporation of the solvent and extraction in pentane (Table 1, entry 7). The silylated ester **1** was clearly characterized by its ¹H and ¹³C NMR spectra and its infrared spectrum (ν (C=O): 1743 cm^{−1}) (see ESI†).

In these reactions, the nature of the solvent plays an important role. Ethers, alcohols, amines or any compound with carbonyl functions can not be used as solvent as they can react with Me₃SiI.^{28,29} Solvents are also not anodyne on the fate of the reaction as observed by replacing dichloromethane (bp = 40 °C, ϵ = 8.93) with acetonitrile which has higher boiling point and polarity (bp = 82 °C, ϵ = 37.5). With 2 equiv. Me₃SiI at 100 °C, the depolymerization of PCL in MeCN-*d*₃ appeared a little faster (5 h, 90% in **1**) than in CD₂Cl₂ (5 h, 74% in **1**) as evidenced in the entries 6 and 8 of Table 1. However, in these conditions, acetonitrile induced a loss of selectivity and formation of the acyl iodide I(CH₂)₅CO₂I (**2**) according to the ¹H and ¹³C NMR spectra (see ESI†). Compound **2** is obtained by the deesterification of **1** with Me₃SiI and is concomitant with the release of hexamethyldisiloxane ((Me₃Si)₂O, observed by ¹H NMR, see ESI†). Increasing the temperature to 130 °C and 150 °C for a mixture containing 2 equiv. Me₃SiI sped up the formation of **2** with an increase of the 2/1 ratio from 17/83 to 32/68 (Table 1, entries 9–10).

Acyl iodides (RCO₂I) are valuable compounds as they are the most reactive acyl halide species and only a few synthetic methods have been developed for their preparation.^{30–32} For example, Jung *et al.*²⁰ briefly mentioned (but did not provide any experimental details) the thermal treatment of the monoesters RCO₂R' with Me₃SiI in chlorinated solvents (CCl₄, CHCl₃). However, Olah's group contradicted this claim, as the authors did not detect the formation of acyl iodide, probably due to shorter reaction times.³³ In 1990, Keinan *et al.* demonstrated the effectiveness of Me₃SiI in chloroform to convert carboxylic acids and esters RCO₂R' (R = alkyl; R' = H, alkyl) to the corresponding silylesters (RCO₂SiMe₃) and that the reaction was significantly accelerated by iodine (I₂), likely *via* the formation of the stable triiodide anion. Unfortunately, the resulting RCO₂SiMe₃ products were not further converted into the acyl iodide derivatives RCO₂I except in a few cases, in very low amounts (< 5%). Using diiodosilane (SiH₂I₂) and I₂ instead of Me₃SiI/I₂ enhanced the deesterification of silylesters to acyl iodides.³²

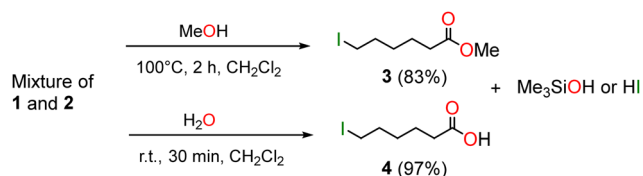
To accumulate compound **2**, a MeCN mixture of PCL containing an excess of Me₃SiI (6 equiv.) was monitored by



^1H NMR. After 16 h at 150 °C, the 1/2 ratio was equal to ca 23/74 and did not change after further heating for 17 h (Table 1, entry 11). Inspired by Keinan *et al.*, **PCL** was treated with excess of a 1 : 1 mixture of $\text{Me}_3\text{SiI}/\text{I}_2$ and led after 10 h at 150 °C in CD_2Cl_2 to a mixture of **1** and **2** in a 23/77 ratio (Table 1, entry 12). This ratio did not improve with further heating (see ESI†). In CH_2Cl_2 , I_2 effectively increased the formation of **2** but did not yield pure **2**. Under these conditions, acetonitrile was not suitable, as it reacted with **2**. Therefore, compound **2** could not be obtained pure by these two methods.

The above reactions (Table 1) revealed that the depolymerization of **PCL** into **1**, with Me_3SiI , is quite rapid (and selective in CD_2Cl_2) but the transformation of **1** to **2**, even with the mixture $\text{Me}_3\text{SiI}/\text{I}_2$, is a more difficult step and isolation of pure **2** by this route seemed unlikely. Such a mixture of **1** and **2** can however be upgraded to the ester $\text{I}(\text{CH}_2)_5\text{CO}_2\text{Me}$ (**3**) by immersing it in dry methanol. After 3 h at 100 °C and evaporation of the alcohol, the ^1H NMR spectrum showed the presence of **3** as the only species. It was isolated in a yield of 83% and the NMR data (^1H and ^{13}C , see ESI†).³⁴ Similarly, hydrolysis of the above mixture of **1** and **2** in CH_2Cl_2 led after 30 min at room temperature to $\text{I}(\text{CH}_2)_5\text{CO}_2\text{H}$ (**4**) isolated after usual work-up as a white powder in an excellent yield of 97% (Scheme 2).³⁵

We also examined SiH_2I_2 for the transformation of **PCL** to **2**. In presence of an excess SiH_2I_2 (5 equiv.) at 150 °C, ^1H NMR monitoring revealed the complete denaturation of **PCL** into a mixture of **1'** and **2** which progressively evolved into 1,6-diodohexane (**5**) and *n*-hexane (**6**). The ability of SiH_2I_2 to engage in both iodide and hydride transfers is novel and we further confirmed this reactivity by the reduction of 2-iodobutane with SiH_2I_2 (see ESI†). In CD_2Cl_2 , after 15 h at 150 °C, **PCL** was transformed into a mixture of **1'** and **2** without any reductive product (Table 2, entry 1). After 120 h, **1'** and **2** have been almost completely converted into **5** and **6**. In MeCN, within similar conditions, an intractable brown solid deposited after 1 h and the ^1H NMR spectrum was complex and not informative (Table 2, entry 2). Solvent-less reaction of **PCL** suspended in SiH_2I_2 proved interesting (Table 2, entry 3). After 4 h at 150 °C, the ^1H NMR spectrum (in CD_2Cl_2) showed a complex mixture of **1'** (44%), **2** (40%), **5** (8%) and **6** (8%), which then evolved to only **5** (56%) and **6** (44%) after 17 h. Colorless crystals of SiI_4 were obtained from this mixture,³⁶ evidencing reduction of **5** with SiH_2I_2 . This reaction unveiled the reductive capacity of SiH_2I_2 which can, without any catalyst, both cleave C–O bonds of **PCL** to depolymerize it into carboxylic monomers (**1'** and **2**) and deoxygenate the resulting acyl iodide **2** into diiodohexane (**5**) and *n*-hexane (**6**). We also checked that in these conditions



Scheme 2 Methanolysis and hydrolysis of a mixture of **1** and **2**.

Table 2 Depolymerization of **PCL** with SiH_2I_2 : optimization of the reaction conditions^a

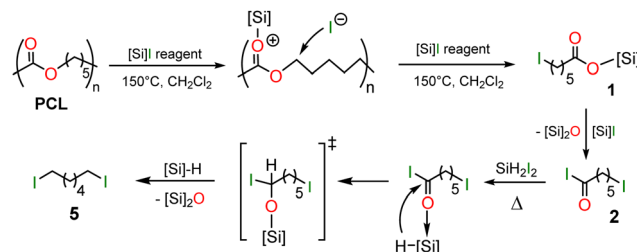
Entry	Solvent	<i>t</i> (h)	Yield ^b (%)			
			1'	2	5	6
1	CD_2Cl_2	15	53	42	0	0
		120	1	2	35	~50
2	CD_3CN	1	Degradation			
3	None ^c	4	44	40	8	8
		17	0	0	56	44

Equiv. of SiH_2I_2 given per monomeric fragment $\text{C}_6\text{H}_{10}\text{CO}_2$. ^a Conditions: **PCL** (0.28 mmol with respect to the monomer unit), solvent (0.4 mL). ^b Yields in **1'**, **2**, **5** and **6** determined by integration of their ^1H NMR signals vs. those of the standard (dodecane or mesitylene). ^c NMR spectrum recorded in CD_2Cl_2 after evaporation of the SiH_2I_2 .

(150 °C, excess SiH_2I_2) both pure **1** and **2** were indeed transformed into **5** and **6** (see ESI†). This reaction is reminiscent of the reduction of aromatic acids and aromatic silyl esters into benzylic trichlorosilanes ($\text{ArCH}_2\text{SiCl}_3$) by HSiCl_3 .³⁷

Compounds **1–6** are relevant molecules in organic chemistry and in materials science. Silyl esters are indeed convenient intermediates for the preparation of functional polymeric substrates such as easily degradable poly(silyl ester)s and extensively used as biodegradable surgical devices, matrices for drug delivery, *etc.*^{38–42} Acyl halide species have a wide spectrum of reactivity as electrophiles and acyl iodides are the most reactive ones.⁴³ Compounds **1–2** and **5** are also convenient synthons toward oxygenated and nitrogenated polymers through coupling reactions with a variety of bifunctional reagents such as amino-acids, hydroxy-acids, diamines, *etc.*⁴⁴

From the experiments and the products characterized above, a plausible mechanism to the formation of **5** from **PCL** can be proposed in Scheme 3. First, **PCL** is depolymerized by Me_3SiI , $\text{Me}_3\text{SiI}-\text{I}_2$ or SiH_2I_2 into the silyl ester **1** or **1'** and then the acyl iodide **2**. This reactivity is related to the strong oxophilic character of the $[\text{Si}]-\text{I}$ reagents which can coordinate carbonyl groups with heterolytic cleavage of the weak Si–I bond. The silylium ion thus generated can induce further carbon–oxygen cleavages in **PCL** to give **1** (or **1'**) and **2**. The coordination of **2** to the



Scheme 3 Proposed mechanism for the reductive depolymerization of **PCL**.



reducing Lewis acid SiH_2I_2 or a hydrosilane derivative (possibly formed in these thermic conditions) strongly enhances the electrophilic character of the carbonyl moiety and favors spontaneous hydride transfer from the proximal hydrosilane. The generated alkoxy silane intermediate, that could not be detected, traps another hydrosilane to give **5** with release of the corresponding disiloxane.

Capitalizing on these results, we next targeted the depolymerization of other polyesters to show the generality of the method. First results evidenced a successful depolymerization of PET (polyethylene terephthalate) from household plastic bottles by treatment (40 h at 150 °C) with excess Me_3SiI in acetonitrile (see ESI†). With this method, the depolymerization of polyesters is currently being optimized and results will be presented in a forthcoming article.

This work highlights the first use of a iodosilane (Me_3SiI) to carry out the efficient depolymerization of a polyester, e.g. polycaprolactone, into functionalized products useful in organic chemistry and in polymer synthesis: silyl ester $\text{I}(\text{CH}_2)_5\text{CO}_2\text{SiMe}_3$ (**1**) and acyl iodide $\text{I}(\text{CH}_2)_5\text{CO}_2\text{I}$ (**2**). Using SiH_2I_2 also offered new possibilities in polyester deconstruction. For example, with **2**, hydride transfer occurred spontaneously to deoxygenate it to diiodohexane $\text{I}(\text{CH}_2)_6\text{I}$ and *n*-hexane. This was the first catalyst-free depolymerization of a polymer with halosilane and halo(hydro)silane. Further works are in progress to deconstruct or reductively depolymerize other pure or household oxygenated plastics.

For financial support, we acknowledge CEA, CNRS, the University Paris-Saclay, and the European Research Council (ERC Consolidator Grant Agreement no. 818260).

Conflicts of interest

There are no conflicts to declare.

Notes and references

- World Economic Forum, Ellen MacArthur Foundation and McKinsey Company, *The New Plastics Economy-Rethinking the future of plastics*, 2016.
- OECD, *Global Plastics Outlook: Economic Drivers, Environmental Impacts and Policy Options*, OECD Publishing, Paris, 2022, DOI: [10.1787/de747aef-en](https://doi.org/10.1787/de747aef-en).
- S. Mandard, *Le Monde*, 2023, 6.
- I. Tiseo, Plastic waste worldwide - statistics & facts, https://www-statista-com.translate.google/?x_tr_sl=en&x_tr_tl=fr&x_tr_hl=fr&x_tr_pto=rq&x_tr_hist=true#topicOverview, accessed April 11, 2023.
- H. Böll, <https://eu.boell.org/sites/default/files/2021-01/Plastic%20Atlas%202019%202nd%20Edition.pdf>, 2019, accessed April 11, 2023.
- The circular economy for plastics, a European overview, <https://plasticseurope.org/wp-content/uploads/2022/06/PlasticsEurope-CircularityReport-2022-2804-Light.pdf>, 2022, 25.
- A. R. Rahimi and J. M. Garcia, *Nat. Rev. Chem.*, 2017, **1**, 0046.
- A. C. Fernandes, *Green Chem.*, 2021, **23**, 7330–7360.
- E. Feghali, L. Tauk, P. Ortiz, K. Vanbroekhoven and W. Eevers, *Polym. Degrad. Stab.*, 2020, **179**, 109241.
- A. Ahrens, A. Bonde, H. Sun, N. K. Wittig, H. C. D. Hammershøj, G. M. F. Batista, A. Sommerfeldt, S. Frølich, H. Birkedal and T. Skrydstrup, *Nature*, 2023, **617**, 730–737.
- A. Kumar, N. von Wolff, M. Rauch, Y. Q. Zou, G. Shmul, Y. Ben-David, G. Leitus, L. Avram and D. Milstein, *J. Am. Chem. Soc.*, 2020, **142**, 14267–14275.
- E. M. Krall, T. W. Klein, R. J. Andersen, A. J. Nett, R. W. Glasgow, D. S. Reader, B. C. Dauphinais, S. P. Mc Ilrath, A. A. Fischer, M. J. Carney, D. J. Hudson and N. J. Robertson, *Chem. Commun.*, 2014, **50**, 4884–4887.
- L. Wursthorn, K. Beckett, J. O. Rothbaum, R. M. Cywar, C. Lincoln, Y. Kratish and T. J. Marks, *Angew. Chem., Int. Ed.*, 2023, **62**, e202212543.
- C. Jehanno, J. W. Alty, M. Roosen, S. De Meester, A. P. Dove, E. Y. Chen, F. A. Leibfarth and H. Sardon, *Nature*, 2022, **603**, 803–814.
- L. Monsigny, J.-C. Berthet and T. Cantat, *ACS Sustainable Chem. Eng.*, 2018, **6**, 10481–10488.
- D. J. Grant and D. A. Dixon, *J. Phys. Chem. A*, 2009, **113**, 3656–3661.
- R. Walsh, in *Bond dissociation energies in organosilicon compounds*, ed. B. Arkles, G. Larson, Gelest Inc., 2008.
- G. A. Olah, S. C. Narang, B. G. B. Gupta and R. Malhotra, *J. Org. Chem.*, 1979, **44**, 1247–1251.
- M. E. Jung and M. A. Lyster, *J. Org. Chem.*, 1977, **42**, 3761–3764.
- M. E. Jung and M. A. Lyster, *J. Am. Chem. Soc.*, 1977, **99**, 968–969.
- M. E. Jung and P. L. Ornstein, *Tetrahedron Lett.*, 1977, 2659–2662.
- H. R. Kricheldorf, *Angew. Chem., Int. Ed. Engl.*, 1979, **18**, 689–690.
- M. E. Jung and M. A. Lyster, *J. Chem. Soc., Chem. Commun.*, 1978, 315–316.
- G. M. Blackburn and D. Ingleson, *J. Chem. Soc., Chem. Commun.*, 1978, 870–871.
- M. A. Woodruff and D. W. Hutmacher, *Prog. Polym. Sci.*, 2010, **35**, 1217–1256.
- M. Labet and W. Thielemans, *Chem. Soc. Rev.*, 2009, **38**, 3484–3504.
- <https://www.alliedmarketresearch.com/polycaprolactone-market-A06096>, accessed april 11, 2023.
- N. Ajvazi and S. Stavber, *Tetrahedron Lett.*, 2016, **57**, 2430–2433.
- F. Wang, M. Qu, X. Lu, F. Chen, F. Chen and M. Shi, *Chem. Commun.*, 2012, **48**, 6259–6261.
- H. M. R. Hoffmann and K. Haase, *Synthesis*, 1981, 715–719.
- M. F. Ansell, *Preparation of acyl halides*, ed. S. Patai, PATAI'S Chemistry of Functional Groups, 1972.
- E. Keinan and M. Sahai, *J. Org. Chem.*, 1990, **55**, 3922–3926.
- T. L. Ho and G. A. Olah, *Proc. Natl. Acad. Sci. U. S. A.*, 1978, **75**, 4–6.
- S. El Fangour, A. Guy, V. Despres, J. P. Vidal, J. C. Rossi and T. Durand, *J. Org. Chem.*, 2004, **69**, 2498–2503.
- The ester $\text{I}(\text{CH}_2)_5\text{CO}_2\text{Me}$ (**3**) and the acid $\text{I}(\text{CH}_2)_5\text{CO}_2\text{H}$ (**4**) are sold by Merck at the respective prices of 310€/g and 964€/g (06-07-2023), Iodotrimethylsilane Me_3SiI is at the price 36€ for 5 g (Merck).
- E. Biehl and U. Schubert, *Monatsh. Chem.*, 2000, **131**, 813–818.
- R. A. Benkeser, E. C. Mozdzen and C. L. Muth, *J. Org. Chem.*, 1979, **44**, 2185–2188.
- D. K. Gilding and A. M. Reed, *Polymer*, 1979, **20**, 1459–1464.
- R. A. Gross and B. Kalra, *Science*, 2002, **297**, 803–807.
- M. Wang, D. Gan and K. L. Wooley, *Macromolecules*, 2001, **34**, 3215–3223.
- M. Cazacu, G. Munteanu, C. Racles, A. Vlad and M. Marcu, *J. Organomet. Chem.*, 2006, **691**, 3700–3707.
- J. M. Weinberg, S. P. Gitto and K. L. Wooley, *Macromolecules*, 1998, **31**, 15–21.
- M. G. Voronkov, N. N. Vlasova, O. Y. Grigor'eva, L. I. Belousova and A. V. Vlasov, *Russian J. Org. Chem.*, 2009, **45**, 486–490.
- F.-R. Zeng, J. Xu, L.-H. Sun, J. Ma, H. Jiang and Z.-L. Li, *Polym. Chem.*, 2020, **11**, 1211–1219.

