



Novel perfluoropolyethers containing 2,2,4-trifluoro-5-trifluoromethoxy-1,3-dioxole blocks: synthesis and characterization

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ABSTRACT

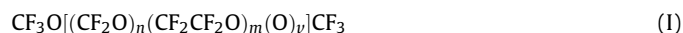
Peroxidic perfluoropolyethers (PFPEs) are industrial intermediates used by Solvay Solexis for the preparation of different classes of (per)fluoropolyethers (Fomblin[®], Galden[®], Solvera[®], Fluorolink[®]). The chemistry of these peroxidic compounds has been recently exploited for the synthesis of novel PFPE block copolymers. In the present work we report the synthesis, the structural and physical–chemical characterization of block copolymers obtained by the reaction of peroxidic PFPEs with 2,2,4-trifluoro-5-trifluoromethoxy-1,3-dioxole, a cyclic homopolymerizable perfluoroolefin. These block copolymers combine the most attractive properties of the PFPEs, like the excellent lubrication, the high thermal stability and the optical transparency, with new specific properties which are related to the perfluorodioxolenic blocks.

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1. Introduction

Perfluoropolyethers (PFPEs) are synthetic fluids largely used as high quality lubricants and also used in heat transfer applications [1]. Their superior performances can be explained on the basis of their unique properties like: chemical and thermal stability, electrical resistance, wide operating temperature range, non-flammability, non-toxicity and zero-ozone-depletion potential.

Among the several routes reported in literature for the synthesis of PFPEs, the process developed by Solvay Solexis is based on the low temperature oxy-polymerization of perfluoro-olefins. In particular, in the case of tetrafluoroethylene (TFE), the product of this reaction is a peroxidic PFPE with the following structure:



The peroxidic units (O)_v of the structure (I), randomly distributed along the chain, can be easily removed by thermal treatment or under UV exposure, thus obtaining a highly stable PFPE, commercially known as Fomblin[®] Z [2].

Photo-oxidation is a very versatile technology that can also be applied for the preparation of functionalized PFPEs by introduction of specific fluorinated co-monomers like 1,3-perfluorobutadiene

[3], perfluoroalkylsulfonyl vinyl ethers [4] and perfluorodioxoles [5]. For example, by using 2,2,4-trifluoro-5-trifluoromethoxy-1,3-dioxole (TTD) as comonomer, a peroxidic PFPE with functional repeating units of the type –CF(OCF₂OC(O)CF₃)O– is obtained [5].

The chemistry of the peroxidic PFPEs has been recently exploited for the synthesis of a new class of “PFPE-based” block copolymers that can be prepared by decomposing the peroxidic units of (I) in the presence of free radical homopolymerizable fluoro-olefins [6]. These new block copolymers are represented by the formula (II):



The A block is a perfluoropolyether moiety composed of –CF₂O– and –CF₂CF₂O– units, whereas B is a perfluoropolyolefinic block whose length depends on the reactivity of the olefins and on the reaction conditions.

These block copolymers combine the most attractive properties of PFPEs and, in particular, the excellent lubrication, the high thermal stability and the optical transparency, with new specific properties which are strictly related both to the composition and to the length of the perfluoropolyolefinic blocks.

In the present work we report the synthesis, the structural and physical–chemical characterization of PFPE–TTD block copolymers obtained by the reaction of the peroxide (I) with TTD, a cyclic perfluoro-olefin of formula (III) that can be prepared in good yields through the hypofluorite technology [7]. TTD is already used for the preparation of amorphous and high molecular weight

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polymers and copolymers (Hyflon[®] AD) whose typical properties are the solubility in fluorinated solvents, high glass transition temperature (T_g), high thermal stability, good optical clarity, and low dielectric constant [8,9].



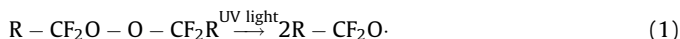
2,2,4-trifluoro-5-trifluoromethoxy-1,3-dioxole (TTD)

These new structures show a low UV absorption, in particular in the region of interest for microlithography, an excellent thermal stability and a glass transition that is tunable with the TTD content in the copolymer. As reported below, these interesting and original properties are due to a combination of the properties typical of TTD copolymers with those of perfluoropolyethers.

2. Results and discussion

2.1. Synthesis of PFPE–TTD block copolymers

Four samples of PFPE–TTD block copolymers were synthesized by exposing a solution of peroxidic PFPE in TTD, kept under stirring, to UV light for some hours (details are reported in the Section 4). In these conditions, the peroxidic links of (I), here indicated as $\text{RCF}_2\text{O}-\text{O}-\text{CF}_2\text{R}$ where R is a PFPE moiety, homolytically decompose and generate two alkoxy radicals [10–13]:



These alkoxy radicals can then undergo β -scission reactions followed by the formation of new alkyl radicals and the evolution of a molecule of carbonyl fluoride:

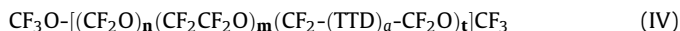


In absence of TTD, the recombination of these radicals leads to a highly stable and non-peroxidic PFPE, whose repeating units are $-\text{CF}_2\text{O}-$, $-\text{CF}_2\text{CF}_2\text{O}-$ and, in minor quantity, $-\text{CF}_2\text{CF}_2\text{CF}_2\text{O}-$ and $-\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{O}-$. In our synthetic experimental approach, however, as TTD is present in the reaction medium, a portion of the radicals formed in (Eq. (2)) react with this olefin and initiate its oligomerization. The reaction mechanism can be described by referring to the classic kinetic scheme of radical polymerizations as reported in Scheme 1:

In the initiation step (Eq. (3)) an alkyl PFPE radical ($\text{R}\cdot$) reacts with TTD, preferably on the position 4 which is the most favourite for both electronic and steric reasons. In fact the carbon radical in (Eq. (3)) is highly stabilized by the presence of two oxygen atoms in alpha position [14,15]. The radical formed in (Eq. (3)) can then grow by addition of other molecules of TTD (Eq. (4)) until the kinetic chain ends by coupling with another radical of the same type (Eq. (5)) or with a PFPE primary radical (Eq. (6)).

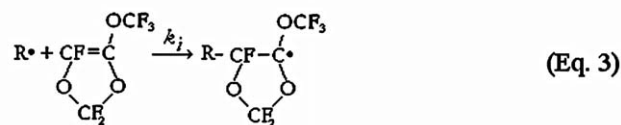
2.2. Characterization of PFPE–TTD block copolymers

The structure of the four samples of the PFPE–TTD block copolymers was determined by ^{19}F -NMR and it can be summarized by the following general formula (IV):

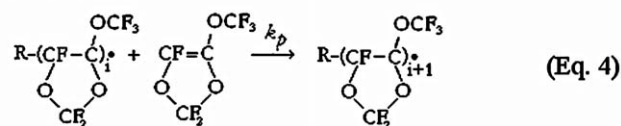


In the structure (IV), $(\text{CF}_2-(\text{TTD})_a-\text{CF}_2\text{O})$ represents the dioxolenic blocks randomly distributed along the chain, “a” is the number of TTD units per each dioxolenic block and “t” is the number of dioxolenic blocks per chain. The structural data of samples 1–4 are reported in Table 1 (see also Section 4.3).

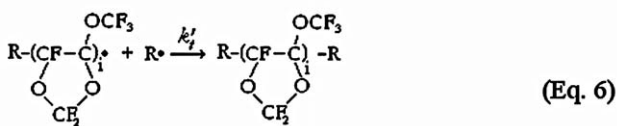
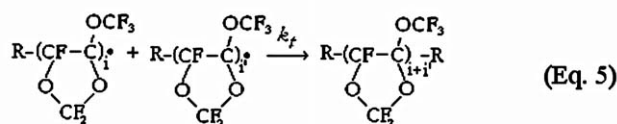
Initiation



Propagation



Termination



Scheme 1. Reaction mechanism of the synthesis of PFPE–TTD copolymer.

Table 2 below reports the intrinsic viscosity of the PFPE–TTD block copolymers measured in Galden[®] D80, an appropriate perfluoropolyether solvent. The Mark–Houwink–Sakurada equation ($[\eta] = KM^\alpha$) is generally used to correlate the intrinsic viscosity $[\eta]$ of homopolymers and statistical copolymers to their molecular weight (M). The parameter α and K of this equation are experimentally determined and are dependent on the polymer–solvent system. For the same solvent, the value of α increases by moving from flexible to rigid polymers.

In the case of the here described PFPE–TTD block copolymers, the Mark–Houwink–Sakurada equation is not applicable to fit the intrinsic viscosity data due to the different structure of the four samples in terms of number and length of the TTD blocks.

Table 1

Structural characterization of the PFPE–TTD block copolymers (IV) determined by ^{19}F -NMR.

Sample	Mn	n	m	a	t	TTD (% by weight)
1	15,000	90	46	1.7	8.0	19
2	19,000	88	45	4.0	8.4	37
3	35,000	105	54	7.2	13.4	58
4	85,000	277	252	12.0	14.2	42

Table 2

Intrinsic viscosity of the PFPE–TTD block copolymers measured at 30 °C in Galden[®] D80. “a” is the number of TTD units per each dioxolenic block and “t” is the number of dioxolenic blocks per chain.

Sample	Mn	TTD ^a (% by weight)	a × t	Intrinsic viscosity (dl/g)
1	15,000	19	14	0.051
2	19,000	37	34	0.060
3	35,000	58	96	0.069
4	85,000	42	170	0.096

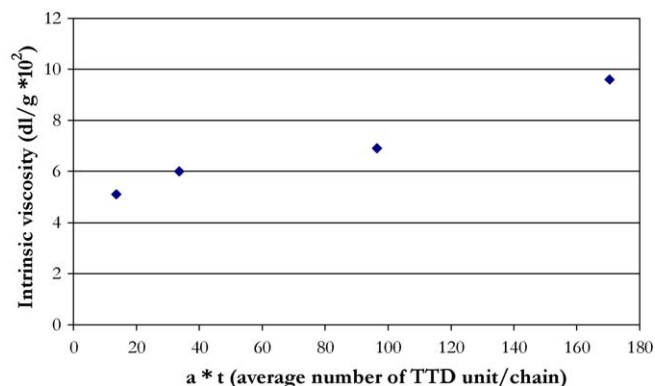


Fig. 1. Intrinsic viscosity of the PFPE–TTD block copolymers as a function of average number of TTD units per chain ($a \times t$).

However, the correlation between the intrinsic viscosity and the molecular weight and between the intrinsic viscosity and the rigidity of the structure is still valid and can be used to discuss the experimental data: in the four samples, the intrinsic viscosity increases with both the molecular weight (M_n) and the TTD content, since the TTD blocks are more rigid, due to the presence of the cyclic units, than the perfluoropolyether blocks. In particular, from sample 1 to sample 2, the increase of intrinsic viscosity seems mainly related to the variation of TTD content as M_n does not increase dramatically. On the contrary, from sample 3 to sample 4, the increase of intrinsic viscosity can be attributed to the variation of M_n as the TTD content decreases. An interesting and empirical correlation is reported in Fig. 1 where the intrinsic viscosity is plotted as a function of the average number of TTD units per chain (column " $a \times t$ " of Table 2). Since the parameter " $a \times t$ " takes into consideration both the TTD content and its block length, there is a direct dependence of the intrinsic viscosity from this parameter.

In Table 3 and in Fig. 2 the glass transition temperatures (T_g) of the PFPE–TTD block copolymers are listed. For each sample, the differential scanning calorimetry (DSC) shows only one glass transition whose value is between those of the PFPE and of the TTD blocks. This is an indication of the absence of segregated phases, for example micro-domains of TTD blocks, being the TTD block perfectly dissolved into the PFPE blocks and vice versa.

The glass transition at infinite molecular weight (T_g^∞) of the perfluoropolyethers is related to the overall oxygen content through the following equation [1]:

$$T_g^\infty (K) = 200 - 80(O/C) \quad (7)$$

In Eq. (7), the O/C parameter is the numerical ratio between oxygen and carbon in the PFPE chain. Hence, the higher the oxygen content, the lower is the glass transition of the perfluoropolyether. By using Eq. (7), for the PFPE blocks of the four block copolymers synthesized, we can estimate a T_g^∞ equal to -133°C for the samples 1 to 3 ($O/C = 0.75$) and a T_g^∞ equal to -127°C for the sample 4 ($O/C = 0.68$). The TTD homopolymer is completely amorphous and has a $T_g = 191^\circ\text{C}$ [16], well above the room temperature. As the two type of blocks display an intimate and

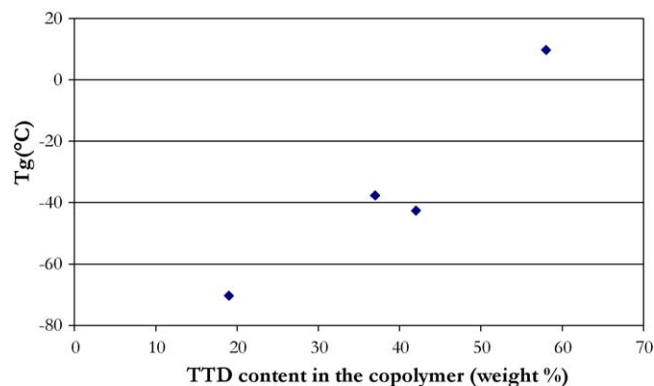


Fig. 2. Glass transition temperature of the PFPE–TTD block copolymers as a function of the TTD content.

uniform mixing, as evidenced by the presence of a unique glass transition, the T_g of the copolymer is intermediate between about -130°C and 192°C and it increases with the content of TTD. By extrapolating the available data, we can estimate a T_g of these copolymer higher than room temperature for the TTD content above 70% by weight.

The results of the thermogravimetric analyses, both in nitrogen and in air, of the four synthesized copolymers are indicated in Table 4. The onset of the decomposition curve (2% weight loss) is comprised between 254 and 346°C (in nitrogen) for the four samples (this broad range of temperature can be explained by supposing the presence of residual peroxidic units in the copolymers, traces of solvent and oligomeric structures), with very small differences between the values obtained in nitrogen and those obtained in air. The perfluorinated structure of these copolymers and the absence of "weak points" in the chain, like hydrogen atoms, double bonds, etc, make the PFPE–TTD block copolymers highly stable in the presence of oxygen at high temperature. As a consequence, the difference between the starting degradation temperature in nitrogen and in air is negligible. Also at temperature higher than 300°C , the effect of oxygen (TGA in air) on the degradation kinetic is slight. The 50% weight loss is substantially identical for all the block copolymers showing a very good thermal stability well above 400°C .

In Fig. 3 the UV absorption spectra of two PFPE–TTD block copolymers (sample 1 and sample 4) are reported in the range between about 155 and 180 nm. For comparison, we have also reported in the same figure the spectra of:

- Fomblin® Z 25, a commercial perfluoropolyether whose formula is $\text{CF}_3(\text{CF}_2\text{O})_n(\text{CF}_2\text{CF}_2\text{O})_m\text{CF}_3$ with $m/n = 0.5$ and $M_n = 9500$. The repeating units of this perfluoropolyether are the same of that of the PFPE blocks in the PFPE–TTD copolymers;
- PTTD homopolymer ($T_g = 191^\circ\text{C}$, Intrinsic viscosity = 20 cc/g)
- Two copolymers of tetrafluoroethylene (TFE) and TTD, one with a molar composition TFE/TTD equal to 20/80 ($M_n = 500,000$) and one equal to 70/30 ($M_n = 700,000$).

Table 4

TGA analyses of the PFPE–TTD block copolymers in nitrogen and in air (data in brackets).

Sample	Temperature (°C) versus percentage weight loss		
	2%	10%	50%
1	295 (293)	377 (364)	434 (420)
2	254 (250)	373 (346)	424 (410)
3	275 (277)	375 (367)	416 (404)
4	346 (331)	389 (375)	430 (415)

Table 3

T_g and ΔC_p of the PFPE–TTD block copolymers determined by DSC analysis.

Sample	T_g (°C)	ΔC_p (J/g °C)
1	−70.3	0.181
2	−37.7	0.168
3	+9.7	0.119
4	−42.6	0.087

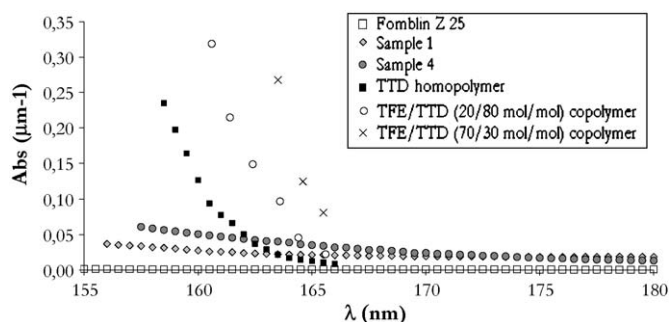


Fig. 3. UV absorption data of some fluorinated polymers.

Electronic transitions between the *highest occupied molecular orbital* (HOMO) and the *lowest unoccupied molecular orbital* (LUMO) are responsible for the absorption in this UV region. For example, the perfluorinated polymers having a backbone made of a sequence of C–C bonds are not transparent since the difference of energy between HOMO and LUMO corresponds to energy associated to this UV region: as evidenced in Fig. 3, the PTTD homopolymer and the TFE–TTD copolymers, being constituted by a chain of C–C bonds, show a very low UV transparency. On the contrary, linear perfluoropolyethers, like Fomblin[®] Z, are known for their exceptional UV transparency: in these compounds the presence of oxygen atoms, every one or two perfluoromethylene groups, significantly increases the energy in the HOMO–LUMO transition, thus lowering the wavelength at which the absorption takes place [17]. The PFPE–TTD copolymers, having both the PFPE and the TTD blocks, shows a behaviour intermediate between that of Fomblin[®] Z and the TTD homopolymer.

3. Conclusion

Peroxidic perfluoropolyether are useful intermediates for the preparation of a new class of PFPE based block copolymers. This versatile synthesis has been applied to the TTD monomer and four different samples of PFPE–TTD copolymers have been prepared and characterized. The two blocks (PFPE and TTD) are perfectly soluble into each other and form a structure that is homogeneous at molecular level, as evidenced by the presence of a unique Tg. The presence of TTD blocks affects some of the typical properties of the perfluoropolyethers by increasing, for example, the viscosity, the glass transition and the UV absorption.

4. Experimental section

Peroxidic PFPEs and TTD are not commercial products and they were synthesized according to the descriptions reported below. Galden[®] HT55 and Galden[®] D80 are perfluoropolyethers with a boiling point of, respectively, 55 and 80 °C produced and commercialized by Solvay Solexis.

4.1. Synthesis of a peroxidic PFPEs

The peroxidic PFPE was obtained by oxidative polymerization of tetrafluoroethylene at low temperature in a fluorinated solvent where elemental fluorine is an efficient free radicals initiator at low temperature [10]. A peroxidic polymeric precursor is formed as result of the polymerization reaction:



The perfluoroether repeating units (–CF₂O– and –CF₂CF₂O–) are interspaced with peroxidic units (–OCF₂CF₂OO– and –

OCF₂OO–). The composition of the polymer and the reaction yields, generally higher than 90%, depend on the temperature and on the tetrafluoroethylene concentration. Carbonyl difluoride and tetrafluoroethylene oxide are the main by-products.

4.2. Synthesis of 2,2,4-trifluoro-5-trifluoromethoxy-1,3-dioxole

TTD was synthesized according to a multi steps methodology based on the addition of CF₃OF to 4,5-dichloro-2,2-difluoro-1,3-dioxole at low temperature, followed by dechlorination with zinc in anhydrous DMF. Details of this preparation methodology are reported in [7].

4.3. Typical procedure for the synthesis of the PFPE–TTD block copolymers

The syntheses of the PFPE–TTD block copolymers were carried out in a photo-chemical reactor which includes an immersion high-pressure Hanau mercury lamp (150 W), a quartz jacket cooled by a cryostat with Galden[®] HT110 fluid and an outer Pyrex cylindrical reactor (volume = 70 cm³). This reactor was provided with magnetic stirring, adjustable cooling system (water), thermocouple, inlet tubes for addition of nitrogen.

A solution of peroxidic PFPE and TTD (boiling point = 26 °C) in Galden[®] HT55 as solvent (the amounts of these compounds are reported in Table 5) is charged into the reactor and cooled, under stirring, at about –30 °C, while a flow of nitrogen (2.0 Nl h^{–1}) is fed into the reactor in order to remove the dissolved oxygen. After about 30 min the UV lamp is switched on and the nitrogen flow is lowered at 0.5 Nl h^{–1}. The reaction is carried out, under stirring, in the temperature range between +10 and +15 °C. At the end the UV lamp is switched off and the solution is discharged from the reactor. The copolymeric product is recovered after distillation of the solvent and of the unreacted monomer. The residual peroxidic content present in the crude products is removed by heating the reaction products under nitrogen at 230 °C for 2 h.

4.3.1. ¹⁹F-NMR analysis

All NMR spectra were recorded at 25 °C, on a Varian INOVA 400 MHz using CFCl₃ as internal standard. Analyses were carried out on solution of PFPE–TTD block copolymers (10% by weight) in hexafluorobenzene. The main signals and their correspondent chemical shifts are reported in Table 6. Since the signals of the –OCF₃ end groups are partially superimposed to the signals of the –OCF₂O– and OCF₃ groups of the dioxolenic units, for the determination of the molecular weight (Mn) of these copolymers we have assumed that the number of –OCF₃ in the final products is equal to the number of –OCF₃ groups in the correspondent peroxidic precursor (where the –OCF₃ groups are easily detectable).

A typical spectrum of PFPE–TTD copolymer is reported in Fig. 4.

The numerical average number of TTD units per blocks (“a”) was calculated on the basis of the ratio between the area of the signal C and the signal D.

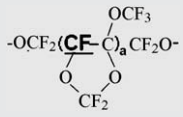
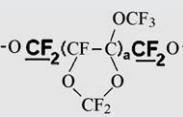
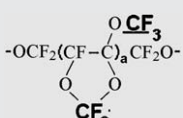
Table 5

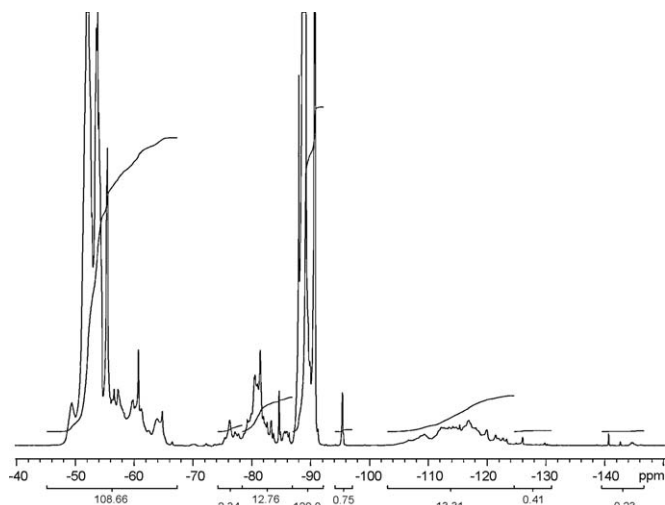
Amount of reactants used for the synthesis of the PFPE–TTD block copolymers. The peroxidic PFPE (I) used for sample 1, 2 and 3 has Mn = 13,000 and 26.0 peroxidic units per chain (2.0 mmol/g). The peroxidic PFPE (I) used for sample 4 has Mn = 43,000 and 29.6 peroxidic units per chain (0.69 mmol/g).

Sample	Peroxidic PFPE (g)	TTD (g)	Galden [®] HT55 (g)	Reaction time (h)
1	6.3	15.8	117.9	5
2	19.8	45.0	75.2	15
3	10.0	130.0	0.0	15
4	10.5	129.5	0.0	15

Table 6

Signal assignment and correspondent chemical shift of the PFPE–TTD block copolymers.

Signal	Structure	Chemical shift (ppm)
A	$-\text{OCF}_2\text{O}-$	$-52 \leftrightarrow -56$
B	$-\text{OCF}_3$	$-56 \leftrightarrow -58$
C	$-\text{OCF}_2\text{CF}_2\text{O}-$	$-88 \leftrightarrow -92$
D		$-105 \leftrightarrow -125$
E		$-75 \leftrightarrow -85$
F		$-48 \leftrightarrow -65$

**Fig. 4.** ^{19}F -NMR spectrum of a PFPE–TTD block copolymer.

4.3.2. Calorimetric analysis

The glass transition temperature of the block-copolymers were obtained using the differential scanning calorimeter Perkin Elmer DSC 2C (calibrated with Indium and cyclohexane). The copoly-

meric samples were cooled at -170°C , and after 3 min at -170°C were heated up to 70°C at the heating rate of $20^\circ\text{C min}^{-1}$. The scans were carried out twice and the T_g was determined as the midpoint of the specific heat (C_p) step with a repeatability of $\pm 0.5\text{ K}$.

The thermogravimetric analyses were carried out with the instrument PYRIS 1 TGA – PERKIN ELMER. The samples were heated from 30°C to 750°C at 10°C/min .

4.3.3. UV absorption

Experimental data were obtained by a series of transmittance measurements on a DUV spectrometer operating in vacuum (10^{-1} torr) in the spectral range 140–180 nm. Atmospheric gases were removed by applying several cycles of freeze (between 80 and 300 K) under vacuum.

4.3.4. Viscosities

Solution viscosities were measured at $30 \pm 0.1^\circ\text{C}$ with a Ubbelohde viscosimeter

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