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Synthesis and characterization of telechelic macromers containing fatty acid derivatives

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ABSTRACT

Telechelic macromers end-capped with (meth)acrylic functionalities are the most commonly used materials in rigid, dental formulations. In order to provide higher flexibility to the final product (not necessarily for dental applications), long chain aliphatic fatty acid derivatives may be chosen. Thus, new telechelic macromers comprising methacrylic functionalities and dimer fatty acid derivatives have been synthesized for the first time, and their chemical structure is discussed in detail. Six different systems comprising ester, anhydride and urethane bonds were synthesized from non-toxic raw materials. FTIR spectroscopy and NMR analysis were used to evaluate chemical structure of new systems. Their molecular masses were estimated from GPC measurements and from an analytical method based on iodine value determination. The latter one proved to be very accurate in determining molecular masses of methacrylated telechelics according to a new method developed in this work. We demonstrated that, via simple organic chemistry, different architectures of telechelic macromers comprising commercially available, long chain derivatives of fatty acid, mainly linoleic acid, with α,ω-dihydroxy, α,ω-dicarboxy or α,ω-diamino functionalities were successfully synthesized. These macromers facilitate the development of new reactive (preferably, photocurable) flexible systems for potential biomedical applications.

1. Introduction

Functional monomers and macromers capable of polymerization (including photopolymerization) have already been used for various applications, including coatings [1–4], adhesives [1,5–7], inks [1,8], photoresists [9–12], and biomedical devices [13–19]. Specifically, photopolymerization is an attractive method, as it proceeds rapidly at ambient conditions and can be controlled with respect to both space and time [20].

The design of photoreactive telechelics for use in medical applications is intensely investigated, predominantly for dental treatment and restoration. Compounds end-capped with (meth)acrylate groups, including bisphenol A diglycidyl ether methacrylate (bis-GMA), triethylene glycol dimethacrylate (TEGDMA) or urethane dimethacrylate (UDMA), are most commonly used in dental formulations [21,22]. Different modifications thereof are being explored with the aim to improve mechanical performance of dental compositions. These studies include the synthesis of aromatic–aliphatic compounds of low molar mass [23–29].

However, for (meth)acrylic telechelics to be more flexible, aliphatic polyethers, such as poly(ethylene glycol) (PEG) [23] or poly(propylene glycol) (PPG) [30], are used. Based on the early research of Priola et al. [31], Wang et al. developed perfluoroether-containing networks for fouling-release coatings [32] and microfluidic devices [33].

Hydrogels derived from telechelic (meth)acrylic macromers are demonstrated to be extremely useful. These macromers are mostly derived from polyethers, poly(ester–ether)s and polycarbonates [13]. PPG- or PEG-based hydrogels are described by Cruise et al. [34] and Jo et al. [35]. In order to tune the material degradation and mechanical performance, co-macromers of PPG/PEG with ε-caprolactone [36,37], α-hydroxyacids [38–40], or aliphatic carbonates [15,41] have been synthesized. Reports on telechelic (meth)acrylic saccharide macromers have also been published [42–44], and reactive polyanhydride networks based on bis(p-carboxyphenoxy)alkanes, aliphatic mono-, di- and triacids, pyromellitic acid imide [16,45] and cinnamic acid [46] have been studied extensively.

However, there are very few reports of telechelic (meth)acrylic macromers containing long chain fatty acids as components. Although acrylates of castor oil have been known for decades [47] and used as thermosets and for the emulsion polymerization of coatings [48], they have not been thoroughly evaluated in regard to their usefulness as reactive, photocurable formulations. There are some reports on reactive derivatives of soybean oil reacted with PCL- and PEG-diacrylates [49,50] or used as matrices for

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nanocomposites [51]. Soybean and castor oils are modified with acrylic acid and aromatic isocyanate, followed by polymerization [52,53]. Black and Rawlins described vegetable oil macromers used for thiol–ene UV-initiated reactions [54]. Some photocurable triglycerides are synthesized by Eren and Kusefoglu via Ritter's addition of acrylamide to double bonds of pendant alkyl chains [55], or via addition of maleate compounds to epoxidized soybean oil [56]. The use of reactive multiacrylates of ricinoleic acid amide for coatings applications has also recently been reported [57,58].

Since vegetable oils have been used for many years in the production of plasticizers, inks, agrochemicals, lubricants [59–61], and most recently biomaterials [62], it is reasonable to synthesize telechelic (meth)acrylic macromers comprising fatty acids for biomedical applications, preferably as liquids susceptible to photocuring reaction and forming flexible materials [63]. Fatty acid derivatives with one (meth)acrylate functionality give linear polymerization products, however fatty acid derivatives with functionalities along the aliphatic chain do not feature a simple enough dependence between the functionality and properties of cross-linked networks. Therefore, instead of using fatty acids, it is reasonable to apply dimerized fatty acids, which allow for receiving products that have α,ω functionalities. Thus, by altering the chain chemical structure (by producing ester, urethane or anhydride bonds) or varying the macromer chain length (and thus influencing the branching point distance in cross-linked network, that is the network density), it is expect to easily tune the properties of cross-linked networks, formed from these new macromers family.

As the first step toward such sophisticated systems, we report in this manuscript the synthesis of new telechelic methacrylic macromers comprising dimer fatty acids derived from C18 unsaturated fatty acids such as linoleic acid derived from vegetable oils. The preparation of a family of dimer fatty acid derivatives is the essential element of novelty of this work. We have synthesized six new materials and we describe herein the synthetic methodology and characterization of these materials using infrared (IR) spectroscopy, nuclear magnetic resonance (NMR) spectroscopy, gel permeation chromatography (GPC) and iodine value (IV) determination.

2. Experimental

2.1. Materials

Methylene chloride (99.9%), purchased from Chempur (Poland), was distilled from calcium hydride and kept over molecular sieves 4 Å. Triethylamine (99.5%) (TEA), purchased from POCH (Poland), was distilled from potassium hydroxide and kept over molecular sieves 3 Å. Trimethylene carbonate (99%) (TMC), purchased from Boehringer Ingelheim, was recrystallized from ethyl acetate, dried in vacuo and flushed with a stream of nitrogen directly prior to use. Dibutyltin dilaurate (95%) (DBTDL), 2-hydroxyethylmethacrylate (97%) (HEMA), isophorone diisocyanate (98%) (IPDI), hexamethylene 1,6-diisocyanate (98%) (HDI), methacryloyl chloride (>97%), 1,4-diazabicyclo[2.2.2] octane (⩾99%) (DABCO) and phenothiazine (>98%) were purchased from Sigma Aldrich and used as received. The reagents for iodine value determination (all of analytical grade) were purchased from Sigma Aldrich and used as received. The α,ω-difunctional derivatives of hydrogenated dimerized linoleic acid (C36), trade name Pripol 1009, Pripol 2033, Priplast 1838 and Priamine 1074, were generously provided by Croda (New Castle, DE, USA and Gouda, The Netherlands). These are difunctional derivatives of C18 fatty acids resulting from dimerization process (thus giving C36 compounds). Some possible structures are shown in Scheme 1 [64,65]. Some of the properties of these materials are summarized in Table 1.

2.2. Syntheses of materials

All reactions were carried out in an inert gas atmosphere and under moisture-free conditions. The detailed description of reaction routes can be found below. All compounds were kept refrigerated after the synthesis. Scheme 2 presents the chemical structures of synthesized macromers.

2.2.1. P2033-DMA (ester)

The compound was obtained in a condensation reaction of Pripol 2033 with methacryloyl chloride. An amount of Pripol 2033 equivalent to 33.6 mmol of hydroxyl groups was introduced to a 100 mL round-bottom flask. Then, methylene chloride was added and after the Pripol dissolved, 40 mmol of triethylamine was added. The reaction mixture was cooled down to 0 °C and stirred for 30 min. Afterward, 37 mmol of methacryloyl chloride was added dropwise over 30 min. The reaction mixture was removed from the ice bath and allowed to warm up to room temperature. Stirring was continued for another 24 h. Then, the reaction mixture was filtered to remove the trimethylammonium salt and subsequently extracted with saturated sodium bicarbonate solution (twice), deionized water (twice) and brine (once). The organic phase was dried over magnesium sulfate and filtered. After adding 100–200 μmol of phenothiazine for each mol of C=C double bond content, the organic phase was evaporated to dryness. The product was a viscous sticky colorless fluid. The yield relative to Pripol 2033 was 70%.

2.2.2. P1838-DMA (ester)

This procedure was analogous to the procedure for P2033-DMA. The product was a viscous sticky slightly yellowish fluid. The yield relative to Pripol 1838 was 75%.

2.2.3. P1009-DMA (anhydride)

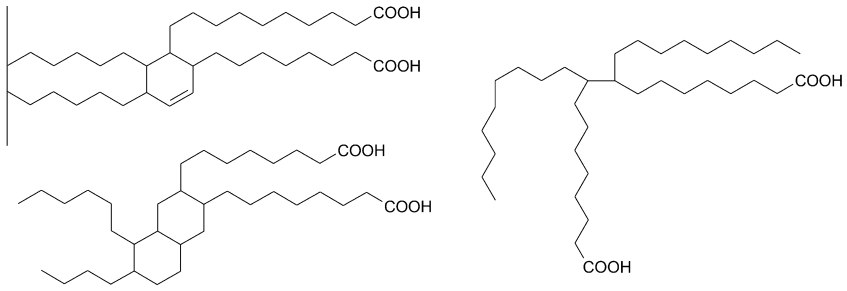
This procedure was analogous to the procedure for P2033-DMA, with the difference that α,ω-carboxyterminated Pripol 1009 was used. The product was a viscous sticky brownish fluid. The yield relative to Pripol 1009 was 60%.

2.2.4. P1838-UR (urethane)

Five mille litter of methylene chloride, 15 mg of DBTDL and 12 mmol of IPDI were introduced to a 100 mL round-bottom flask that was kept in an ice bath. After 30 min of stirring, Pripol 1838 (equivalent to 12 mmol of OH groups) in 20 mL of methylene chloride was added dropwise over 30 min. When the addition was complete, the ice bath was removed and the reaction continued at room temperature until the isocyanate groups stopped decaying. This was determined by tracking the ratio of A_{1534}/A_{2263}, where A_{1534} is the FTIR absorbance at 1534 cm^{-1} (bending N—H vibrations in forming urethane bond) and A_{2263} is the absorbance at 2263 cm^{-1} (N=C=O vibrations in decaying isocyanate groups). When the isocyanate groups stopped decaying, a small amount of DABCO and 25.2 mmol of HEMA were introduced and the bath temperature was raised to 35 °C. The reaction continued until all isocyanate groups were converted, as confirmed by FTIR. Phenothiazine (100 mol ppm with respect to HEMA) was then added to the reaction mixture, the product was precipitated into fivefold excess of ice-cold methanol, washed thoroughly with methanol and the residual solvent was evaporated. The resulting product was a transparent, highly viscous, sticky, colorless liquid. The yield relative to Pripol 1838 was 80%.

2.2.5. P2033-UR (urethane)

The procedure was similar to the procedure for P1838-UR. As a diol and diisoacyanate, Pripol 2033 and hexamethylene 1,6-diisocyanate were used, and as the catalyst only DBTDL was used, that was added at the beginning of synthesis. The product was precipitated

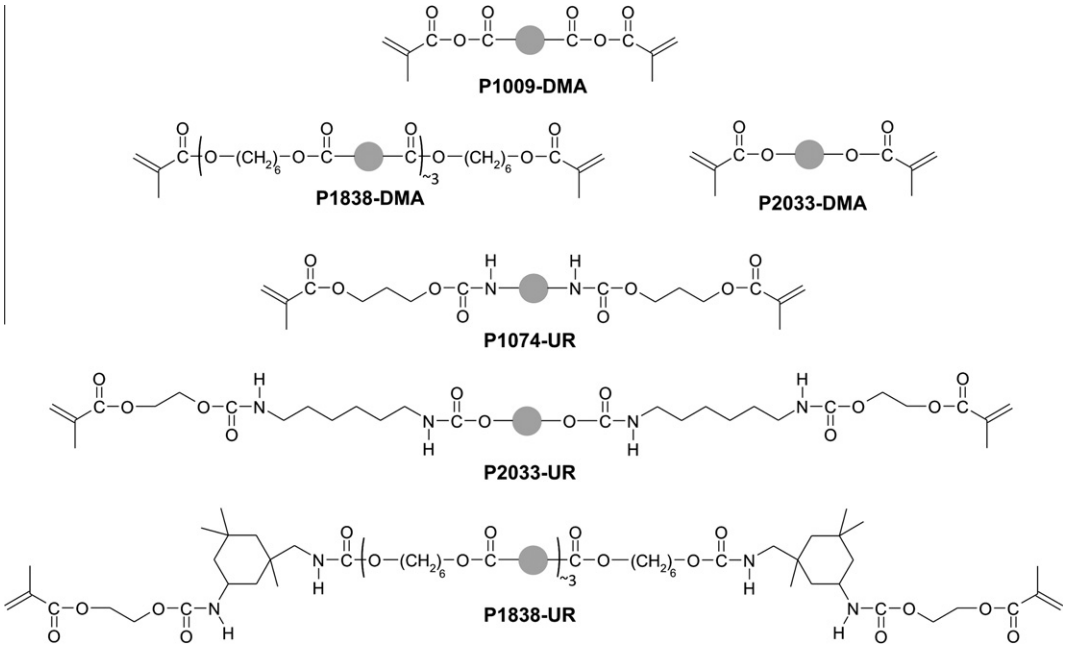


Scheme 1. Examples of the possible structures of dimer linoleic acid. The degree of unsaturation is low. On average, one double bond occurs in more than five molecules.

Table 1
Selected properties of raw materials used for syntheses.

	Functionality	COOH/OH/NH_2 number (mg/g)	Theoretical M_n (g/mol)	M_n (g/mol) from GPC	DI from GPC	Iodine value (g/100 g)
Pripol 1009	COOH, 2	196	572	970	1.04	4.5
Pripol 1838	OH, 2	56	2004	4600	1.52	3.1
Pripol 2033	OH, 2	207	542	920	1.04	3.3
Priamine 1074	NH_2, 2	205	547	770	1.11	5.6

COOH/OH/NH_2 numbers as given by the manufacturer; theoretical M_n calculated from the functionality; DI – dispersity index; conditions of GPC and the method of determining iodine value are given in Section 2.3.



Scheme 2. Chemical structures of synthesized compounds. The grey circle denotes a C36 dimer fatty acid moiety.

into fivefold excess of ice-cold hexane, washed with hexane and dried in vacuo. It appeared as white powder. The yield relative to Pripol 2033 was 95%.

2.2.6. P1074-UR (urethane)

In the first step, Priamine 1074 was reacted with TMC according to the ring opening addition route. 36.6 mmol of TMC were dissolved in methylene chloride and Priamine 1074 equivalent to 36.6 mmol of amine groups was added to the solution. The reaction was carried out at room temperature until the band at 1758 cm^{-1} completely disappeared in the infrared spectrum, which indicated total conversion of TMC. Then the product was precipitated into fourfold excess of hexane, washed four times with 200 ml of hexane and dried in vacuo. The resulting product was a viscous, sticky, yellowish liquid. The yield was 90% with respect to Priamine 1074. The compound obtained in the first step was used as a substrate in the second step. Its hydroxyl number was determined and used for calculating the feed in the second step. An amount of P1074-TMC equivalent to 18.6 mmol of hydroxyl groups was dissolved in methylene chloride and 24 mmol of triethylamine was added. The reaction mixture was cooled down to 0 °C and after 30 min of stirring, 20.5 mmol of methacryloyl chloride was added dropwise over 30 min. The product was isolated as described above for P2033-DMA. The resulting product was a viscous, sticky, dark yellow liquid. The overall yield of the P1074-UR relative to Priamine 1074 was 60%.

2.3. Analytical methods

The infrared spectra were recorded on a Thermo Nicolet NEXUS apparatus (4000–500 cm^{-1}, resolution 4 cm^{-1}, 32 scans). The compound was spread onto a sodium chloride plate and transmission spectra were collected. EZ OMNIC software was used for data processing.

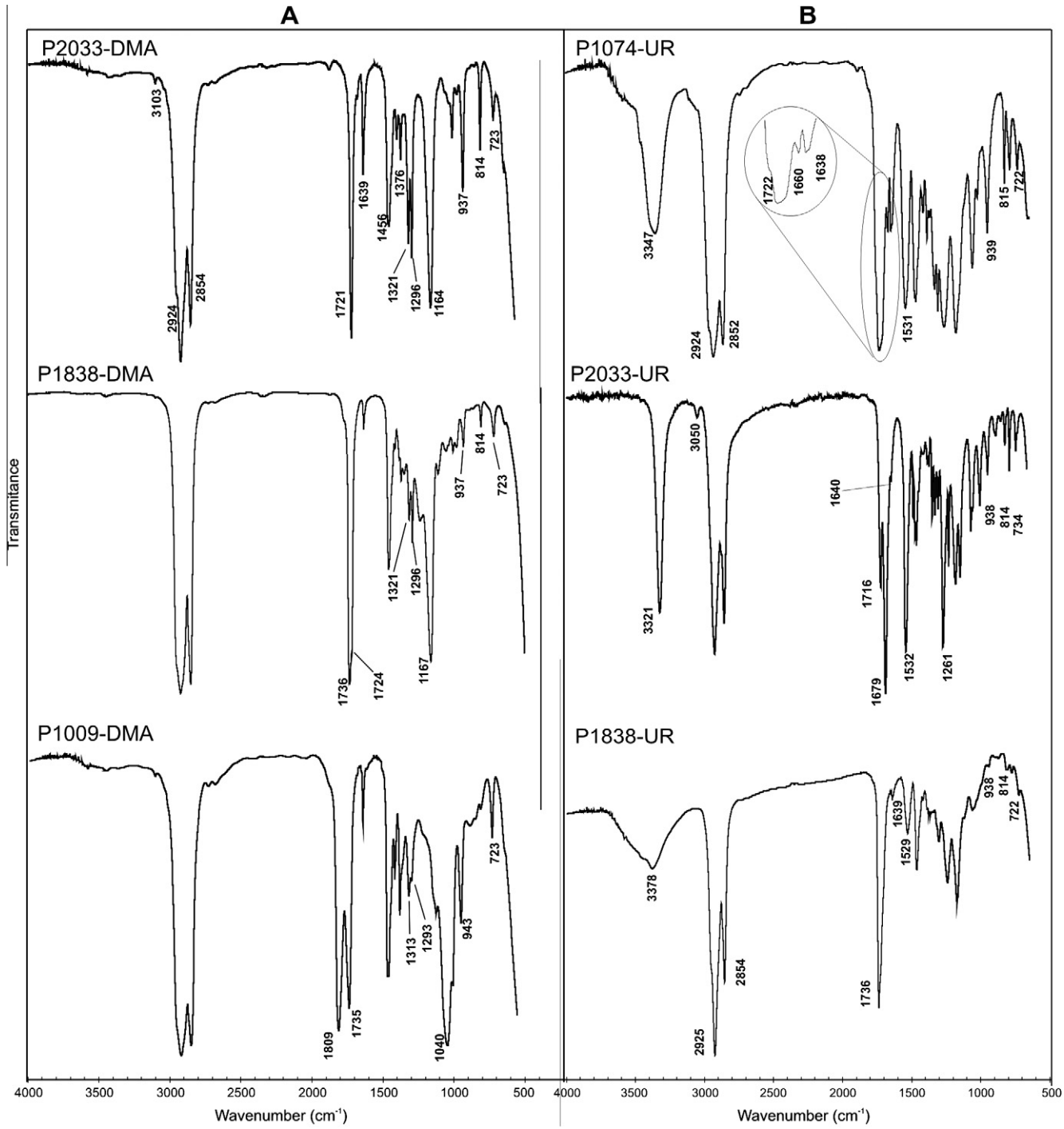


Fig. 1. Infrared spectra of synthesized macromers: (A) telechelics containing ester and anhydride bonds and (B) telechelics containing urethane bonds.

^{1}H and ^{13}C NMR measurements were performed on Varian VNMRS 400 MHz. $CDCl_3$ was used as solvent and all shifts were determined with respect to TMS. MestReNova software was used for data processing.

Iodine value was determined according to PN-EN ISO 3961:2006. Typical procedure is described. 0.5 to 3.0 g of sample was dissolved in the mixture of cyclohexane with acetic acid or methylene chloride. Then, 25 mL of Wijs solution was added and the mixture was left in a dark place for 1 h. Afterwards, 20 mL of aqueous potassium iodide (100 g/L) was added and the iodine formed was titrated with 0.1 M sodium thiosulphate in the presence of starch. A blank analysis was also performed. The iodine value (*IV*), expressed as number of grams of iodine that can bond to 100 g of the analyzed compound [g/100 g], was calculated from the formula:

$$IV = 12.69 \cdot c \cdot (V_1 - V_2)/m, \quad (1)$$

where c – concentration of thiosulphate solution in mol/dm^3; V_1 and V_2 – volumes of thiosulphate solution in mL used in blank and analyzed sample, respectively; and m – mass of the sample. The iodine value was calculated as an average from three replicates.

GPC experiments were performed to determine the molecular mass distribution and dispersity index. The GPC system consisted of a 515 HPLC pump, a 717plus autosampler, and a 410 RI detector (Waters Associates). Two PL gel columns 10^3 and 10^5 Å (Polymer

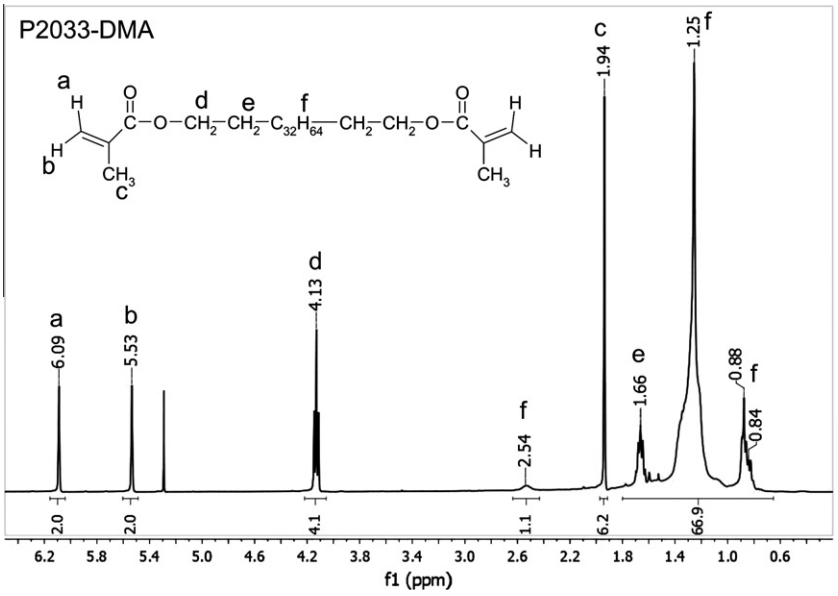


Fig. 2. ^{1}H-NMR spectrum and peaks assignments for P2033-DMA telechelic ester macromer.

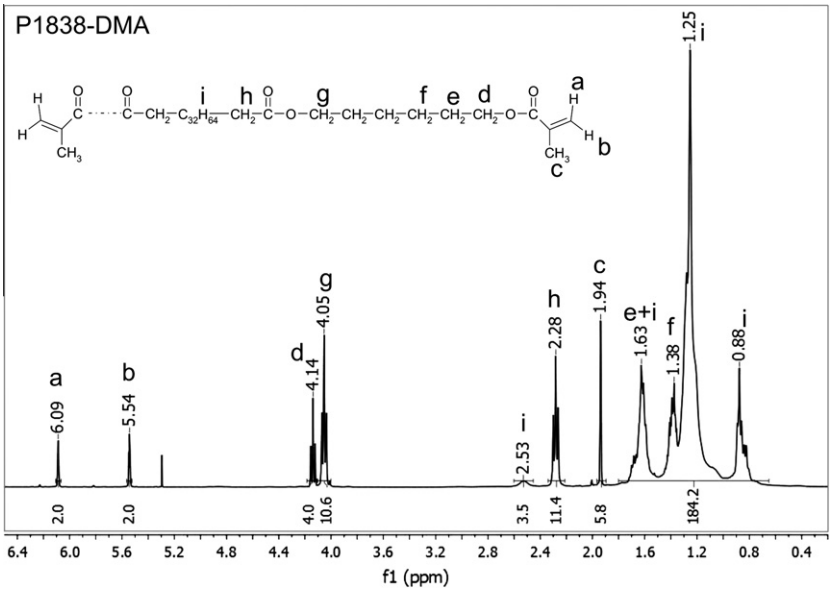


Fig. 3. ^{1}H-NMR spectrum and peaks assignments of P1838-DMA telechelic ester macromer.

Laboratories) were used in series with THF as the mobile phase at a flow rate of 1 mL/min. The samples were dissolved to give a concentration of 10 mg/mL and 20 μL was injected. Waters Associates Empower 2 software was used for data collection and molecular mass calculations. The molecular masses were computed against polystyrene standards of MW 523000, 204000, 96000, 20235, and 7200.

3. Results and discussion

3.1. Infrared spectroscopy

The chemical structures of new telechelic macromers were verified with infrared spectroscopy, the spectra are shown in Fig. 1. Around 3100 cm^{-1} stretching vibrations of C═C—H can be noticed (see Fig. 1A). The bands around 940 and 815 cm^{-1} correspond to bending vibrations of C═C—H. The bands between 1720 and 1740 cm^{-1} reflect the stretching C═O vibrations in ester groups (methacrylate and aliphatic ester bonds inside the core of the compound (see Scheme 2)). The split band with maxima at 1809 and 1735 cm^{-1} for P1009-DMA is characteristic for stretching of C═O in anhydride bond. A split band with maxima around 1290 and 1320 cm^{-1} corresponds to stretching O—C(═O) in esters of α,ß-unsaturated acids, while at 1639 cm^{-1}, the stretching C═C vibrations are noticed. Bands around 1165 cm^{-1} (esters) and 1040 cm^{-1} (anhydride) both correspond to stretching C—O—C(═O).

For the three urethane macromers (Fig. 1B), all the bands characteristic for methacrylated compounds are also present, just like for telechelics containing ester and anhydride bonds. The new bands typical for urethanes can be found in Fig. 1B: the bands around 3350 cm^{-1} for stretching N—H vibrations in urethane groups, 1530 cm^{-1} of bending N—H in urethane groups. In the spectra of

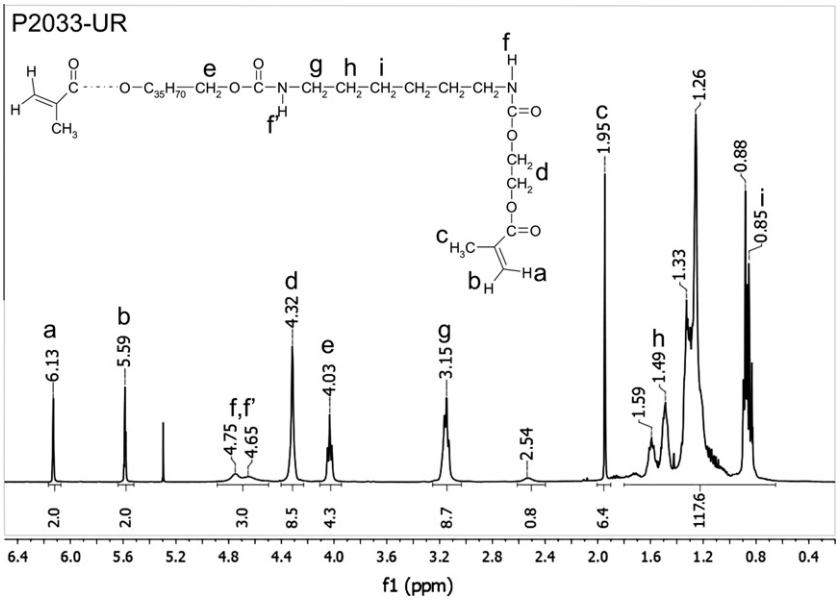


Fig. 4. ^{1}H-NMR spectrum and peaks assignments of P2033-UR telechelic urethane macromer.

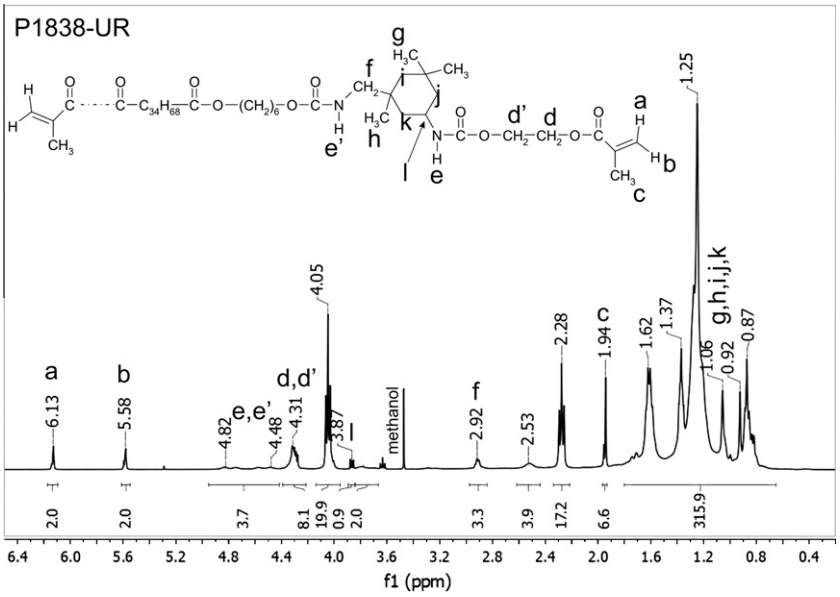


Fig. 5. ^{1}H-NMR spectrum and peaks assignments of P1838-UR telechelic urethane macromer.

P1074-UR and P2033-UR, where the concentration of urethane groups is higher, a distinct band at 1660–80 cm^{-1} corresponding to stretching C=O vibrations in carbamate is observed.

3.2. NMR

Chemical structure of new materials was also verified with NMR spectroscopy and the results with peaks assignments are presented in Figs. 2–6. The peaks without assignments correspond to solvents (methylene chloride at 5.29 ppm, methanol 3.5–3.6 ppm, some hexanes below 1.2 ppm.

The analysis of NMR spectra confirmed that synthesized materials show expected chemical structure. As can be seen from Fig. 2, telechelic macromer containing terminal methacrylic groups and symmetrical ester groups was synthesized from Pripol 2033. Similar structure, with methacrylic functionalities and ester bonds was found for P1838-DMA telechelic macromer as depicted in Fig. 3. As can be noticed from Figs. 4–6, peak assignments clearly indicate formation of urethane bonds in methacrylate-terminated telechelics. An interesting observation was noticed for P1009-DMA macromer, namely the disproportionation of the mixed anhydride bonds as evidenced in Fig. 7 showing ^{1}H-NMR and ^{13}C-NMR spectra of P1009-DMA.

As proven by Tarcha et al. [66], mixed dianhydrides of methacrylic acid and linear diacids are labile compounds and are likely to undergo disproportionation on workup and storage, within a few days. The disproportionation reaction scheme is presented in Scheme 3, showing the formation of an oligomeric anhydride and a symmetric anhydride.

As evidenced by ^{1}H and ^{13}C-NMR analysis, this disproportionation has occurred also in the case of P1009-DMA telechelic anhydride macromer.

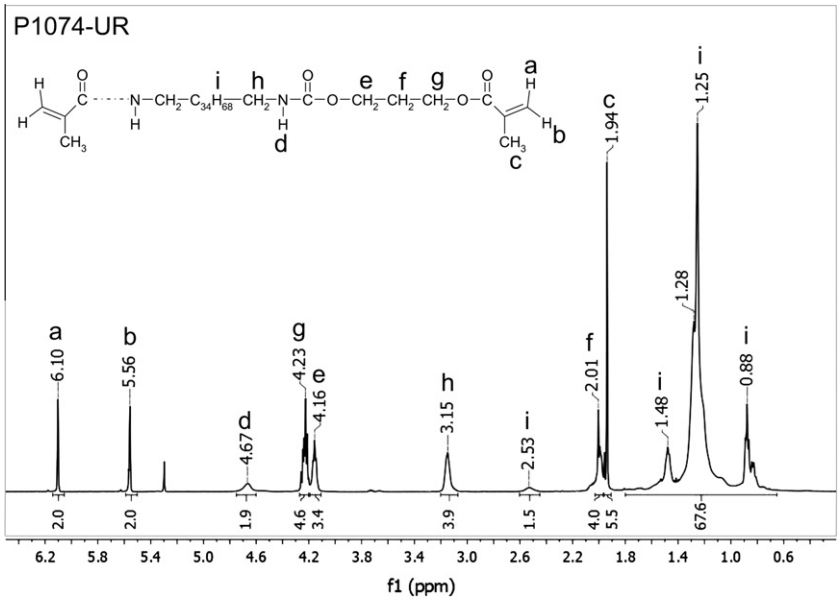


Fig. 6. ^{1}H-NMR spectrum and peaks assignments of P1074-UR telechelic urethane macromer.

3.3. GPC

The results of GPC analysis are presented in Fig. 8 and in Table 2. The obtained molecular masses should be used only for comparison and not as absolute values. The GPC was calibrated using polystyrene (PS) standards and the molecular weights of standards used were much higher than those of the telechelic macromers. The structure of PS is vastly different from the branched structures of the telechelic macromers, which contributes to inaccurate results [67]. The inaccuracy of the molecular masses will be discussed further in Section 3.4.

As shown in Table 2, the macromers P2033-DMA, P2033-UR, P1074-UR and P1009-UR were obtained from monodisperse starting materials, whereas the starting materials used for synthesizing P1838-DMA and P1838-UR were already a mixture of oligomers. For all macromers, an increase in molecular mass relative to raw materials is observed. The dispersity remains unchanged for P2033-DMA and P1074-UR. However, for the materials obtained from Pripol 1838 (P1838-DMA and P1838-UR) the DI decreases due to the elimination of lower oligomers in the purification process. For P1009-DMA and P2033-UR the DI raises and moreover the chromatograms are multimodal plots. In the case of P2033-UR, high DI can result from the reaction between a diol and diisocyanate, where all groups have equal reactivity, and formation of oligomers is unavoidable. The reason for the observed multimodality for P1009-DMA was already discussed in Section 3.2. The GPC results confirm the formation of anhydride oligomers due to disproportionation.

3.4. Iodine value

Iodine value measures the degree of unsaturation of a compound. It is expressed as the mass of iodine capable of bonding to 100 g of the analyzed compound. In this work, a novel application of this parameter is proposed, namely calculating molecular mass of telechelic compounds. To the best of our knowledge, use of the iodine value to determine molecular weight has not yet been reported in the literature.

The iodine value of a α,ω-dimethacrylated compound can be given as:

$$IV = 50,760/M + N, \tag{2}$$

where N is a component coming from the native unsaturation of the compound. The contribution of the native iodine value is inversely proportional to the molar mass increase upon the synthetic procedure leading to a telechelic compound and hence Eq. (2) can be written as:

$$IV_2 = 50,760/M_2 + IV_1 \cdot (M_1/M_2), \tag{3}$$

where M_1 is the molar mass of the compound before the synthesis, M_2 is the molar mass of the telechelic compound, IV_1 and IV_2 are the iodine values of the compounds before and after the reaction, respectively. For compounds having several core moieties in their structure (i.e. P1838-UR) Eq. (3) must be modified by factor f, which equals the average number of core moieties per one synthesized molecule. Then the final equation is given as:

$$IV_2 = 50,760/M_2 + IV_1 \cdot (M_1/M_2) \cdot f, \tag{4}$$

which after rearrangement gives the final formula (4):

$$M_2 = (f \cdot M_1 \cdot IV_1 + 50,760)/IV_2 \tag{5}$$

This equation is valid for all macromers, to which two terminal double bonds are introduced upon the synthesis (for example, for α,ω-dimethacrylated compounds). For compounds with other functionalities, multiplying 50,760 by $F/2$ is sufficient (where F is the number of telechelic double bonds in the particular compound). Eq. (4) has been proved very accurate in theoretical calculations for molecular systems of both mono- as well as oligomeric compounds.

The key factor f is determined from integration of ^{1}H-NMR spectra. The spectra of the macromers were compared with those of raw materials (not shown here) and the factor f was calculated. For the spectra of the macromers, it was assumed that the integral value of 2.0 for each of the double bond methylene protons in methacrylate group corresponds to one macromer molecule. The accuracy of the calculations proves to be high for the macromers where f theoretically equals 1 (P1838-DMA, P2033-DMA, P1074-UR), its calculated values are very close to 1 (see Table 3).

A clear disagreement of molecular mass values obtained from GPC and calculated from iodine value is observed (see Fig. 9). The results obtained from GPC always have considerably higher values. The inaccuracy of GPC results was explained in Section 3.3. The question now arises about the accuracy of calculations based on iodine value and Eq. (4). Again, it can be assessed with the help of

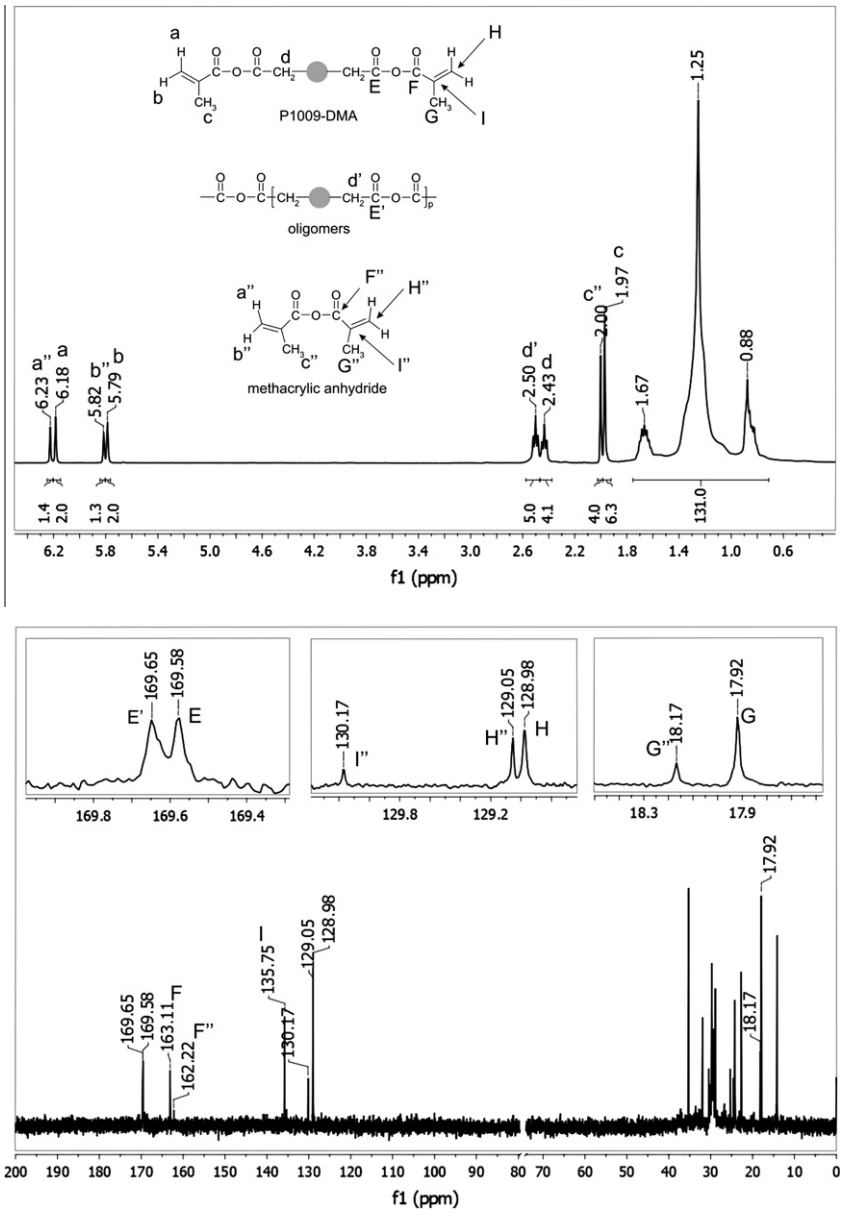
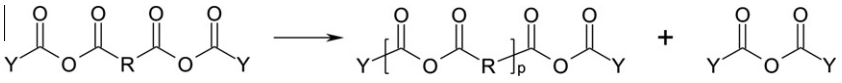


Fig. 7. ^{1}H and ^{13}C-NMR spectra and peaks assignments of P1009-DMA telechelic anhydride macromer.



Scheme 3. Schematic representation of disproportionation of mixed anhydrides.

macromers that form no oligomers, but whose compounds are built plainly by adding groups to ends of the core, which are P1838-DMA, P2033-DMA and P1074-UR. The molecular mass of these compounds can be calculated theoretically from atomic masses of elements. Table 3 compares theoretical molar masses with those calculated from Eq. (4). It is clearly seen that the molecular mass values obtained from Eq. (4) are very close to the theoretical ones and thus much closer to the actual values than the data from GPC (Table 2). This method, based on iodine value determination, is useful for molecular mass determination of telechelic macromers and oligomers containing reactive (meth)acrylate endgroups.

4. Conclusions

New functional telechelic methacrylic macromers comprising ester, anhydride and urethane bonds can be synthesized from commercially available, long chain derivatives of fatty acid, mainly linoleic acid. Derivatives with α,ω-dihydroxy, α,ω-dicarboxy or α,ω-diamine functionalities were used as a "core" to build up different architectures via simple organic chemistry. The anhydride macromer undergoes disproportionation thus forming an oligomeric anhydride and a symmetric anhydride. Evaluation of molecular masses of new systems based on GPC measurements indicated no increase in the dispersity index for the systems comprising ester

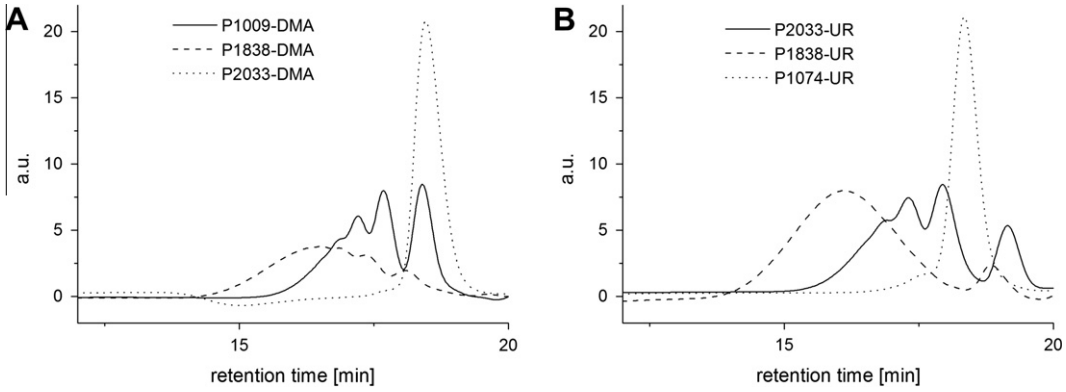


Fig. 8. Chromatograms of synthesized macromers: (A) telechelic ester and anhydride macromers and (B) telechelic urethane macromers.

Table 2
GPC results of synthesized macromers. DI – dispersity index.

	M_n (g/mol)	M_n (g/mol) of starting material	DI	DI of starting material
P1009-DMA	1910	572	1.22	1.04
P1838-DMA	5960	2004	1.39	1.52
P2033-DMA	1040	542	1.05	1.04
P2033-UR	2550	542	1.32	1.04
P1838-UR	12,560	2004	1.21	1.52
P1074-UR	1210	547	1.09	1.11

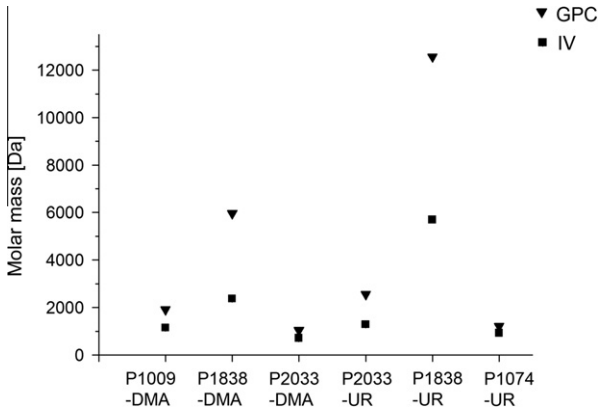


Fig. 9. Molecular mass values of the macromers obtained from GPC (number average, ▼) and calculated from Eq. (4) (■).

bonds and for the urethane system derived from the diamine derivative of fatty acid and trimethylene carbonate (TMC). An analytical method (iodine value determination) combined with a new formula accurately determined molecular mass of methacrylated telechelics for the first time.

The new telechelic macromers reported here represent a first step toward development of reactive (preferably, photocurable) systems for biomedical applications. These systems will be reported in future papers.

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Table 3
Results of iodine value determination and of related calculations (Eq. (4)).

	f	IV_1 (g/100 g)	M_1 (g/mol)	IV_2 (g/100 g)	M_{IV} (g/mol)	M_{theor} (g/mol)
P1009-DMA	2.18	4.5	572	49	1150	–
P1838-DMA	0.91	3.1	2004	23.8	2370	2140
P2033-DMA	1.06	3.3	542	74.2	710	678
P2033-UR	1.52	3.3	542	41.7	1282	–
P1838-UR	1.46	3.1	2004	10.5	5698	–
P1074-UR	0.98	5.6	547	58.1	925	887

f – the average number of core moieties per one macromer molecule, as calculated from ^{1}H-NMR; IV_1 – iodine value of the raw materials (cf. Table 1); M_1 – molecular mass of the raw material (cf. Table 1); IV_2 – iodine value of the macromer; M_{IV} – molecular mass of the macromer calculated from Eq. (4); M_{theor} – theoretical molecular mass.

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