Study on polymerization of bio-based isosorbide monomethacrylate for the formation of low-T and high-T sustainable polymers

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Study on polymerization of bio-based isosorbide monomethacrylate for the formation of low-T_g and high-T_g sustainable polymers.

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Abstract

Isosorbide monomethacrylate (IMMA) is a biobased monomer that appears as a potential substitute for current petrobased methacrylates to prepare high-performance sustainable polymers by free-radical polymerization technique. However, as the molecular weight of polymers can markedly affect their physical, mechanical and processing properties, it is crucial to understand the nature of the processes that control the growing of IMMA based polymer chains. To this end, the free radical polymerizability of IMMA has been investigated in depth under various conditions (solvent, conversion rate, [IMMA]/[AIBN] ratio). This study, based on the determination of chain transfer constants using the Mayo method, highlighted the key role of monomer and solvent transfer reactions for controlling molecular weight of PIMMA ($C_{tr}M$ = 5.0x10^{-4} ; $C_{tr}S$ (DMSO) = 4.0x10^{-4}; $C_{tr}S$ (DMF) = 5.0x10^{-4}; $C_{tr}S$ (Isopropanol/dioxane (1:6)) = 1.0x10^{-3}). Knowing the parameters governing the free radical polymerization of IMMA, PIMMA with tailored molecular weight (from 2100 to 80200 g.mol^{-1}) and T_g have been prepared and characterized. In particular, DSC analyses of PIMMA revealed the opportunity to prepare from low-T_g to high-T_g materials with different potential applications.

Keywords: Isosorbide, radical polymerization, polymethacrylate, transfer constant.

1. Introduction

Bio-based polymers and materials continue to be extremely investigated to substitute their petro-based counterpart in myriad of applications. In this context, isosorbide is without any doubt the most used sustainable product.[1] Indeed, this starch derivative has already proven to be an excellent precursor for the formation of high-performance polymers thanks to its rigid bicyclic structure.[2] However, even if isosorbide has the particularity to contain two secondary alcohols in *endo* or *exo* position displaying different reactivities, [3] the vast majority of the polymers developed contain isosorbide in their main chains. This type of structure prevents post-modifications such as the formation of 3-D networks or the

incorporation of other functions of interest.[4–7] In the area of isosorbide-based polymers, only few studies describe the radical chain-growth polymerization of monomers with isosorbide as pendant groups[8–10] and, surprisingly, only three publications report the radical homopolymerization of monovinyl-substituted isosorbide containing one of two free alcohol function.[11–13] For example, Drockenmuller has described the RAFT polymerization of 1-vinyl-4-isosorbide-1,2,3-triazole leading to the formation of homopolymers with good thermal properties (T_g of 71 °C and 118 °C for *endo* and *exo* form respectively).[11] On their side, Jannasch et al. have published the radical polymerization of the *exo* stereoisomer of isosorbide monomethacrylate (IMMA) obtained by an enzymatic and highly regioselective approach.[12] Contrary to Drockenmuller, all homopolymers whether they contain the *endo* or *exo* IMMA displayed the same high T_g of 167 °C. Unfortunately, the macromolecular parameters (DP$_n$, M$_n$, Đ) were not determined and, thus, structure-property relationships of polymers were not established. Recently, we have developed the conventional radical polymerization of a diastereoisomeric mixture (exo/endo (66/34)) of isosorbide monoacrylate (IMA).[13] In this study, thanks to the Mayo method, we have highlighted the importance of the transfer constants to monomer and to solvent for controlling the macromolecular properties of PIMA. This fundamental investigation was essential to determine the best conditions to obtain polymers with interesting thermal properties. Finally, thanks to the presence of many free hydroxyl functions, we obtained high performance thermosets by cross-linking with renewable anhydride (T_g = 116 °C and E'= 4 GPa).

This previous study prompts us to investigate the polymerizability of isosorbide monomethacrylate as the presence of methyl groups could allow to obtain polymers with higher T_g than those of PIMA. In this study, we have developed a novel one-step synthesis of IMMA monomer featuring a mixture of *endo/exo* diastereoisomers. The complete study on polymerization of this mixture was investigated under several conditions to determine the transfer constant (C$_{tr}$M) to IMMA monomer thanks to the Mayo method. This fundamental investigation has allowed to know the best conditions to obtain high-T_g sustainable polymers carrying pendent hydroxyl groups.

2. Experimental Section

2.1 Materials

Isosorbide Polysorb P was kindly donated by Roquette Frères. It was dried under vacuum at 40°C overnight before use. Methacrylic anhydride was purchased from Alfa Aesar and was used without purification. Scandium triflate, sodium bicarbonate, azobisisobutyronitrile were purchased from Sigma Aldrich. Acetonitrile, ethyl acetate and isopropanol were purchased from VWR chemicals. Dichloromethane was purchased from Fischer, dioxane from Merck,

dimethylformamide from Carlo Erba and dimethylsulfoxide from Alfa Aesar. NMR solvents ($CDCl_3$ and DMSO-D_6) were purchased from Eurisotop.

2.2. Instrumentation

NMR spectra were recorded on a Bruker Avance III HD, 300MHz, spectrometer and chemical shifts are given in ppm.

Size exclusion chromatography (SEC) analyses were performed on a Waters system equipped with Styragel columns HR4E and HR3 coupled with refractive index (RI) detector. DMF was used as eluent and standards chosen were a range of PMMA from 2180 g.mol^{-1} to 106000 g.mol^{-1}.

DSC and TGA analyses were done on a TA Q100 and a TA Q50 respectively. Pans/lids used were standard aluminum hermetic pans/lids. All DSC analyses were made with the same program: a first heating rate up to 250 °C at 10 °C/min to remove water traces, a cooling rate to -20°C and a second heating rate up to 250 °C at 10 °C/min. T_g were analyzed during the second heating.

2.3. Synthesis of isosorbide monomethacrylate (IMMA)

Isosorbide (1.5 eq, 0.34 mol, 50 g), methacrylic anhydride (1 eq, 0.23 mol, 35.2 g), and Sc(OTf)$_3$ (8.84x10^{-5} eq, 2.03x10^{-2} mmol, 10 mg) were dissolved in 500 ml of acetonitrile and the solution was stirred vigorously at room temperature. After 4 h, the mixture was diluted with dichloromethane and was washed with a solution of saturated sodium bicarbonate and pure water. After drying over MgSO$_4$ the solvent was removed under reduced pressure and the crude product was purified by flash chromatography using C18 stationary phase column and a mixture of methanol/water (5:5) as eluent. Isosorbide monomethacrylate was isolated as a transparent liquid with a yield of 32%. Isosorbide monomethacrylate contain both endo-substituted and exo-substituted isosorbide.

Endo and Exo mixture:

^{1}H NMR, 300 MHz, 25°C, CDCl3 (ppm): 6.15 (1H, s, *Endo*) ; 6.13 (1H, s, *Exo*) ; 5.62 (1H, s, *Endo*) ; 5.61 (1H, s, *Exo*) ; 5.27 (1H, m, *Exo*) ; 5,2 (1H, m, *Endo*) ; 4.90 (1H, t, *J = 5 Hz, Endo*) ; 4.64 (1H, t, *J = 4.6 Hz, Exo*) ; 4.51 (1H, d, *J = 4.1 Hz, Exo*) ; 4.42 (1H, d, *J = 4.7 Hz, Endo*) ; 4.35 (1H, d, *J = 2.6 Hz, Endo*) ; 4.31 (1H, q, *J = 5.9 Hz, Exo*) ; 4.10 (2H, m, Exo) ; 3.90 (1H, Dd, *J$_D$ = 9.2 Hz, J$_d$ = 5.5 Hz, Exo*) ; 3.90 (5H, m) ; 3.57 (1H, *dd 9.6 Hz, J = 5.9 Hz, Exo*) ; 1.96 (3H, s, *Endo*) ; 1.93 (3H, s, *Exo*).

^{13}C NMR, 75 MHz, 25°C, CDCl$_3$ (ppm): 18.2 (*Exo*); 18.5 (*Endo*); 70.9 (*Endo*); 72.3 (*Exo*); 73.5 (*Exo*); 73.6 (*Exo*); 74.5 (*Endo*); 75.7 (*Endo*); 76.5 (*Endo*); 78.6 (*Exo*); 80.8 (*Endo*); 82.0

(*Exo*); 85.7 (*Exo*); 88.5 (*Endo*); 126.5 (*Endo*); 126.6 (*Exo*); 135.7 (*Endo*); 135.8 (*Exo*); 166.3 (*Exo*) 166.8 (*Endo*).

2.4. General procedure for conventional free radical polymerizations

All the polymerizations were made with the same procedure: In a schlenk tube, IMMA and AIBN (All quantities are shown in the Tables S1 and S2 (ESI)) were dissolved in various anhydrous solvents (DMF, DMSO or a mixture of iPrOH/dioxane (1:6)) and three freeze-pump-thaw cycles were carried out. Then the mixture was stirred at 90°C under nitrogen and small samples were taken during the polymerization to determine the monomer conversion by ^{1}H NMR and the molecular weight (M_n) by SEC. At the end of the polymerization, the crude products were precipitated in diethyl ether to obtain white powder. The dried polymers were characterized by NMR spectroscopy, SEC, DSC and TGA.

3. Results and discussion

3.1. Synthesis of IMMA monomer.

IMMA was synthetized by using Sc(OTf)$_3$ as catalyst. Indeed, this Lewis acid has a good stability toward air and water allowing to carry out the synthesis at room temperature and atmosphere.[14] The reaction between methacrylic anhydride and isosorbide was carried out in the presence of an excess of isosorbide to reduce the proportion of dimethacrylate derivative. This procedure led to an interesting conversion of methacrylic anhydride of 62%. During this reaction, *endo*-form is produced in majority (64%) and only 32% of *exo*-form and 4% of isosorbide dimethacrylate are created (Scheme 1). The stereoselectivity observed can be explained by the difference in reactivity of isosorbide alcohols. Indeed, it is well established that the hydroxyl group in position *endo* is more nucleophilic than the one in position *exo*.[15] After purification by flash chromatography, a mixture of diasteroisomers is obtained with an acceptable yield of 32% and the proportion of *exo* and *endo* forms is maintained.
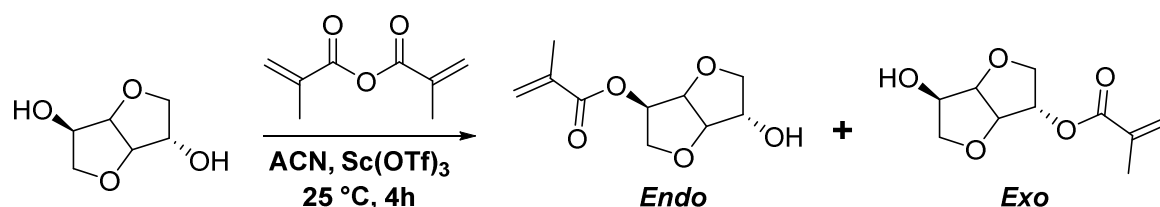

Scheme 1. Synthesis of isosorbide monomethacrylate (IMMA).

3.2 Polymerization of IMMA in various conditions.

Firstly, the free radical polymerization of IMMA was initiated at 90 °C in bulk using AIBN. However, like many (meth)acrylates, the high intrinsic reactivity of IMMA led to insoluble materials.[13,16] The same behavior was also observed with solvents displaying a low transfer constant to solvent ($C_{tr}S$) like dioxane or cyclohexane.[17] Consequently, the polymerization has to be carried out in media featuring higher $C_{tr}S$. For this reason, DMSO, DMF and a iPrOH/dioxane (1/6) mixture were chosen as they show $C_{tr}S > 1\times10^{-4}$.[13,18–21] In a previous study on isosorbide acrylate, different percentages of isopropanol in mixtures were tested (1:1 ; 1:3 and 1:6) but no significant differences in polymerization rate or molecular weights were noted. Therefore, for this study, we only investigated one iPrOH/dioxane ratio (i.e. 1:6). The influence of the nature of the solvent on the polymerization of IMMA was first evidenced by performing kinetic studies. In figure 1.A, one can notice that the initial polymerization rate of IMMA is strongly influenced by the nature of the solvent. Specifically, the highest polymerization rate is observed in DMSO following by the DMF and finally in I/D (1:6) mixture. This observation can be attributed to the transfer constant to solvent. Indeed, DMF is known to display a $C_{tr}S$ higher than the DMSO and isopropanol has the capacity to transfer radicals to its central carbon, reducing the active radical concentration and thus the polymerization rate.[20] As expected for free radical polymerization of methacrylates[22], the highest molecular weights (M_n max) are reached at low conversion. However, depending on the solvent, different M_n max are obtained (70000 g.mol^{-1} in I/D mixture, 71000 g.mol^{-1} in DMF and 119900 g.mol^{-1} in DMSO) suggesting the importance of the chain transfer to solvent for controlling M_n max.
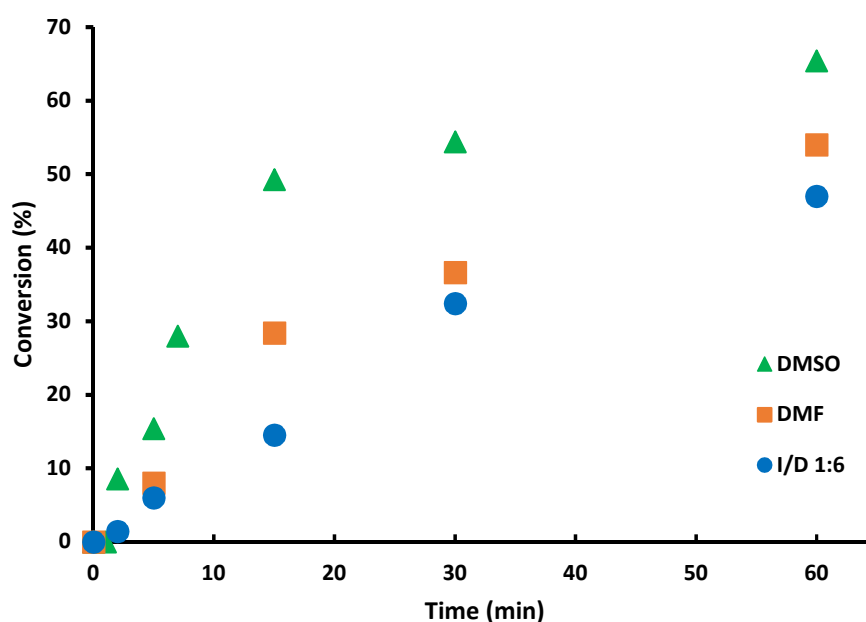

(A)
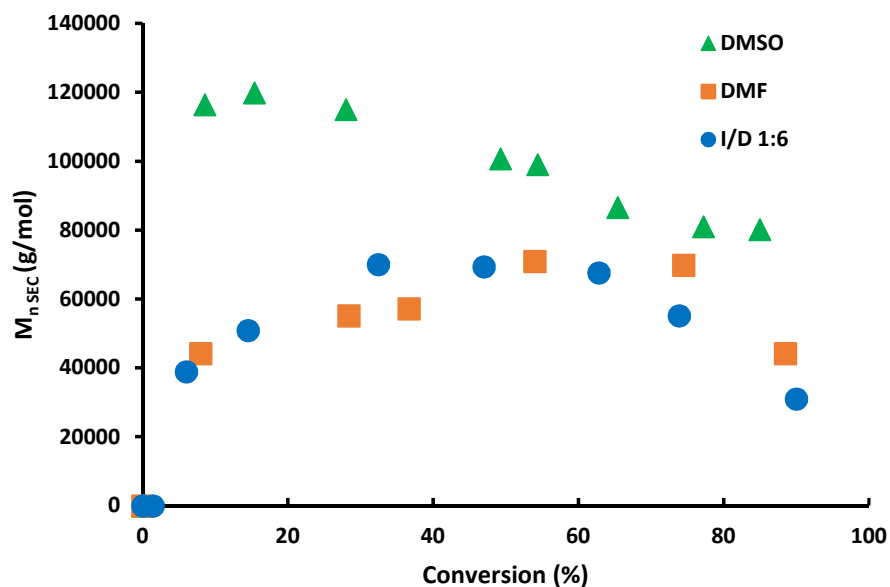
(B)

Fig. 1. Initial conversion versus time (A) and M_n versus conversion (B) for free radical polymerization of 1.4M IMMA ([IMMA]/[AIBN]=200) at 90 °C.

Concurrently, the impact of the monomer/initiator ratio on the M_n was also studied (Fig. 2). As expected, regardless of the [IMMA]/[AIBN], the M_n at high conversion (>90%) are similar and sway around 30000 $g.mol^{-1}$. However, the [IMMA]/[AIBN] ratio has an impact on the M_n max observed. Indeed, when the [IMMA]/[AIBN] ratio increases from 100 to 500, the M_n max rises from 58900 to 115200 $g.mol^{-1}$. A further increase of the [IMMA]/[AIBN] ratio up to 10000 has no impact. This behavior is characteristic of conventional radical polymerization of (meth)acrylates analyzed by SEC.[22,23] where the chain-growth is extremely rapid at the beginning of the polymerization and the molecular weight is controlled by the chain transfer to monomer, leading to the formation of long-chain polymers.[24] Then, as the [Monomer]/[Initiator] ratio decreases, the formation of lower molecular weight chains is privileged and the molecular weight is controlled by the chain transfer to solvent. These two phenomena lead to a decrease of the relative M_n observed by SEC at high conversion.
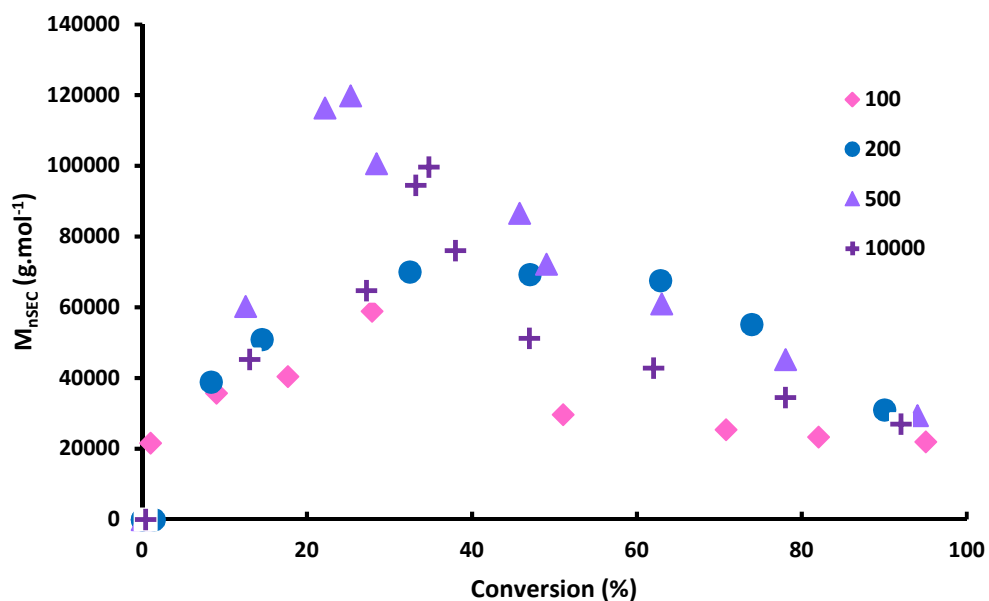
Fig. 2. M_n versus conversion for free radical polymerization of 1.4M IMMA in isopropanol/dioxane (1:6) mixture at 90 °C using different [IMMA]/[AIBN] ratio.

Surprisingly, this trend has not been observed during the polymerization of isosorbide monoacrylate (IMA) in the same conditions.[13] where a plateau has been obtained for M_n, regardless the solvent or the [IMA]/[AIBN] ratio investigated. In that case, the molecular weight was found to be controlled by the chain transfer to monomer ($C_{tr}M = 1.4 \times 10^{-3}$) and the Trommsdorff effect, that both allowed to keep the M_n constant until the end of the conversion. For IMMA, we hypothesized that the decrease of M_n might arise from a low $C_{tr}M$, leading to a control of the M_n by chain transfer to solvent exclusively. To demonstrate this hypothesis, the $C_{tr}M$ to IMMA and the $C_{tr}S$ to DMSO, DMF and I/D (1:6) were determined.

*3.3 Determination of $C_{tr}M$ and $C_{tr}S$*

The transfer constants to monomer and to solvent can be evaluated from the Mayo equation (equation 1).[25] where DP_n and DP_0 are respectively the observed and the theoretical degrees of polymerization. However, methacrylates are known to proceed with high propagation rates and prone to transfer to polymer when they are polymerized via a free radical polymerization process. Hence, DP_0 can be considered as infinite or extremely elevated [26–28] and the $1/DP_0$ term can be thus neglected in equation 1 to obtain equation 2. By plotting $1/DP_n$ as a function of the [Solvent]/[Monomer] ratio at low conversion (<5%), it is possible to determine the transfer to solvent ($C_{tr}S$) and to monomer ($C_{tr}M$) constants.

$$\frac{1}{DP_n} = \frac{1}{DP_0} + C_{tr}M + C_{tr}S\frac{[S]}{[M]} \qquad Equation\ 1$$

$$\frac{1}{DP_n} = C_{tr}M + C_{tr}S\frac{[S]}{[M]} \qquad Equation\ 2$$

Figure 4 shows the Mayo plot for polymerizations carried out in DMSO, DMF and I/D (1:6) mixture. Straight lines were obtained with reasonable linear regression ($R^2>0.97$), confirming the validity of the assumptions that were made in establishing equation 2 and the application of the Mayo method for the determination of transfer constants. The slope of straight lines and intercepts allowed the estimation of $C_{tr}S$ and $C_{tr}M$ transfer constants, respectively. The $C_{tr}S$ obtained are in good agreement with the literature.[29] Indeed, the lowest constant was observed for DMSO (4×10^{-4}), preceded by DMF (5×10^{-4}) and the iPrOH-based mixture shows the highest $C_{tr}S$ (1×10^{-3}). Regarding the $C_{tr}M$, constants values of 5×10^{-4} in DMSO, 4×10^{-4} in DMF and 6×10^{-4} in the I/D mixture are obtained giving an average value of 5×10^{-4}. The $C_{tr}M$ for IMMA is three times lower than the $C_{tr}M$ obtained for isosorbide monoacrylate ($C_{tr}M = 1.4 \times 10^{-3}$).[13] This observation can be explained by the stability of the radical on the tertiary carbon formed during the polymerization of IMMA. This stability can reduce the transfer to monomer comparing to isosorbide monoacrylate (IMA).
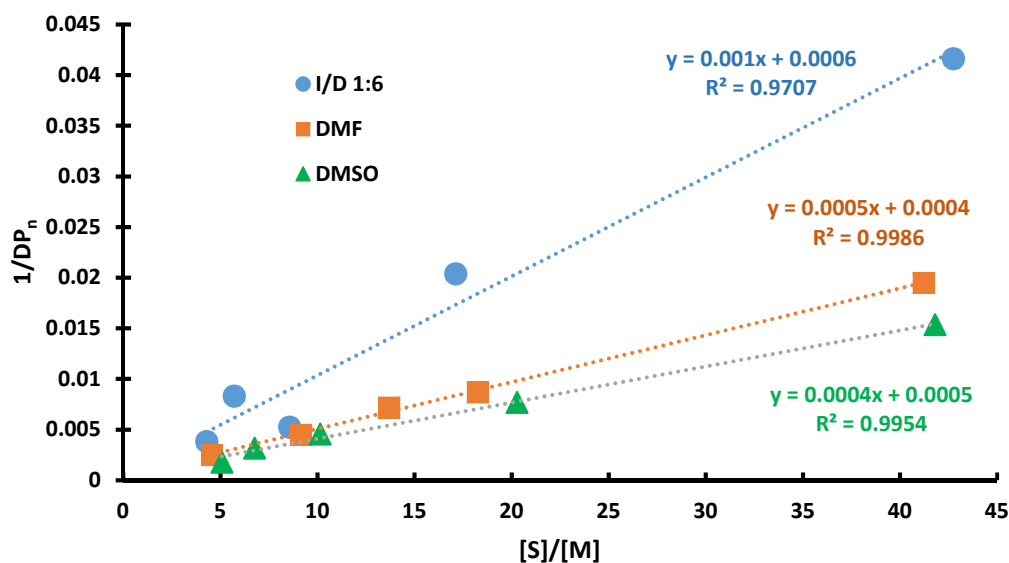
Fig. 3. Mayo plot for free radical polymerization of IMMA ([IMMA]/[AIBN] = 200; conversion <5%) in different solvents at 90 °C.

The $C_{tr}M$ and the $C_{tr}S$ are almost identical in DMF and DMSO and the $C_{tr}S$ is two times higher than the $C_{tr}M$ in iPrOH-based mixture (table 1). Since in our conditions, the initial [Solvent]/[Monomer] ratio is 8.5 ([IMMA]=1.4M), the molecular weight is undoubtedly controlled by the transfer to solvent. These results explain the decrease of M_n obtained at high conversion regardless of the conditions of polymerization.

Table 1. Transfer to solvent ($C_{tr}S$) and to monomer ($C_{tr}M$) constants obtained by the Mayo plot for free radical polymerization of IMMA at 90 °C.

Solvent	$C_{tr}S$	$C_{tr}M$
DMSO	4.0×10^{-4}	5.0×10^{-4}
DMF	5.0×10^{-4}	4.0×10^{-4}
I/D (1:6)	1.0×10^{-3}	6.0×10^{-4}

3.4 Characterizations of PIMMA

Steric exclusion chromatography (SEC) analyses were performed to monitor the evolution of M_n of PIMMA as a function of IMMA conversion. At low conversion (<60%), polymers with dispersities lower than 1.7 are formed (Fig. 4) and dispersities inscrease to 2 when conversion reach to 80%. However, at the end of the polymerization (conversion > 90%), an increase of the dispersities up to 10 is observed. In the literature, an increase of dispersity up to 2 is usually mentioned at high conversion in conventional radical polymerization. This behavior is mainly due to the predominance of the transfer to solvent and the formation of low molecular weight chains. In this study, higher dispersities are observed, probably due to additional chain terminations.[30]
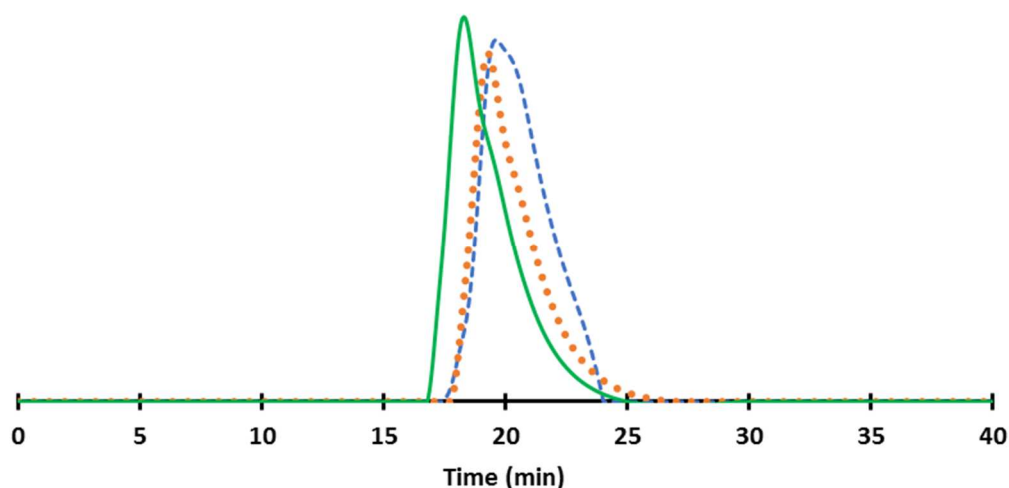
Fig. 4. SEC traces of PIMMA obtained by free radical polymerization in DMSO (green solid line), DMF (orange dotted line) or I/D (1:6) mixture (blue dashed line) at 90 °C ([IMMA]/[AIBN] = 200)

Table 2. Results for free radical polymerization of 1.4M IMMA at 90 °C ([IMMA]/[AIBN] = 200)

Exp.	Solvent	Conv. (%)	M_{nSEC} (g.mol^{-1})	Đ
1	DMSO	42	100700	1.4
2	DMSO	85	80200	2.2
3	DMSO	93	53700	>10
4	DMF	32	69900	1.7
5	DMF	89	44200	2.1
6	DMF	95	18200	>10
7	I/D (1:6)	34	55200	1.6
8	I/D (1:6)	80	34200	2.9
9	I/D (1:6)	96	25500	>10

Finally, thermal properties of PIMMA were investigated by Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA). TGA analyses (Figure S4) showed a weight loss starting from 280 °C and a thermal decomposition starting from 400 °C. In light of these results, DSC analyses were carried out from 20 °C to 250 °C. DSC results reported in Table 3 clearly show the molecular weight dependence of the T_g of PIMMA with T_g values ranging from 28 °C to 175 °C for the range of PIMMA studied (from 2100 to 80200 g.mol^{-1}) (Figure 5 and table 3). Interestingly, the highest molecular weight PIMMA (M_n = 80200 g.mol^{-1}) features a higher T_g than other poly(meth)acrylates like atactic PMMA ($\Delta T_{gPIMMA-PMMA}$= +70 °C) [31] and ,specially, than acetylated isosorbide methacrylate-based polymers (PAMI) with comparable molecular weight (M_n =88900 g.mol^{-1}, $\Delta T_{gPIMMA-PAMI}$ = +45 °C) reported by Reineke [8]. We previously reported that polyisosorbide monoacrylate (PIMA) forms hydrogen bonds thanks to their free alcohol groups, increasing the impact of the M_n on the T_g.[13] This behavior is undoubtedly present in the case of PIMMA.

Table 3. Glass transition temperatures of PIMMA observed as a function of the molecular weight average.

M_{nSEC} (g.mol^{-1})	DPn (SEC)	T_g (°C)
2100	10	28
3600	17	63
4900	23	116
6000	28	118
48400	226	151
80200	374	175
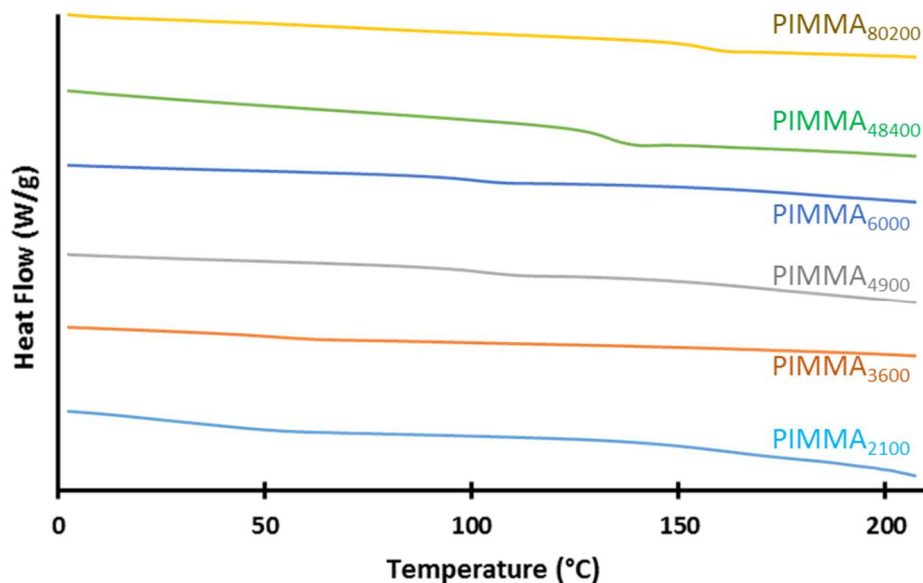
Fig. 5. DSC profiles of PIMMA obtained by free radical polymerization

4. Conclusion

Bio-based isosorbide monomethacrylate (IMMA) has been investigated during free radical polymerization of polymethacrylates featuring free alcohol functions. The transfer constant to monomer were determined thanks to the Mayo method and this fundamental study allowed us to obtain PIMMA, a sustainable polymer, featuring low-T_g (28 °C) to high-T_g (175 °C). In future works, the free alcohol functions will be modified to implement PIMMA in a plethora of domains by incorporating functions and molecules of interest or by forming high performance thermosets.

Data availability

The raw/processed data required to reproduce these findings cannot be shared at this time due to technical or time limitations.

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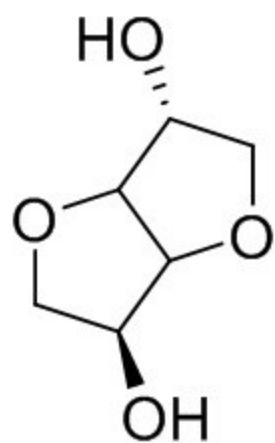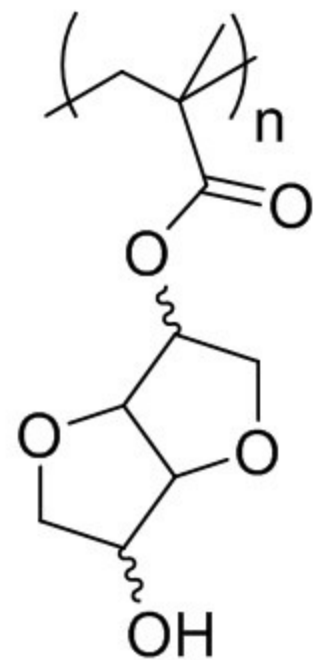
Methacrylic anhydride

Sc(OTf)$_3$
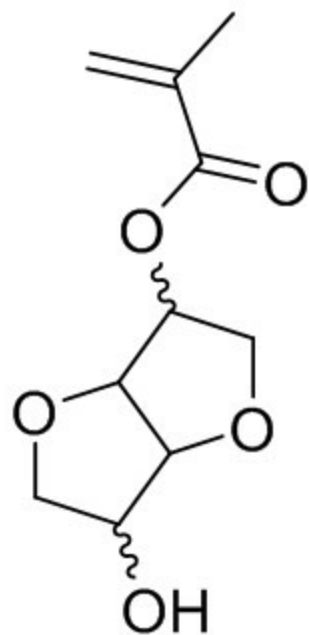
Free radical polymerization

$C_{tr}M$ and $C_{tr}S$

Isosorbide

IMMA
endo and *exo* mixture

Low-T_g and High-T_g PIMMA