Synthesis and characterization of amphiphilic graft copolymers of poly(1,3 dioxolane) macromonomers with styrene and methyl methacrylate

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Abstract: Methacrylate-terminated Poly(1,3 dioxolane) (PDXL) macromonomers were synthesized by cationic ring-opening polymerization in the presence of 2-hydroxypropyl methacrylate (2-HPMA) as transfer agent. Molecular weights, polydispersity index and functionality of the PDXL macromonomers were evaluated by size exclusion chromatography (SEC) and ¹H nuclear magnetic resonance spectroscopy (¹H-NMR). Copolymerizations of PDXL macromonomers, of different molecular weights, with styrene (St) and methyl methacrylate (MMA) were carried out using various feed molar ratios. The resulting polymers confirmed the grafting of PDXL with PS and PMMA by SEC and ¹H-NMR. Monomer reactivity ratios between the macromonomers and the comonomers were estimated from the copolymerization results. Macromonomer reactivity depends on the comonomer considered. Glass transition temperatures of the copolymers were found to decrease with an increase in the amount of PDXL in the copolymers. The values of T_g depend on the composition and the size of the PDXL grafts.

Introduction

Amphiphilic block and graft copolymers consisting of hydrophilic and hydrophobic parts have been subjects of numerous studies, within which block and graft copolymers containing hydrophilic polyoxyethylene segments and other hydrophobic segments have attracted much attention, because polyoxyethylene segments are not only hydrophilic, but also nonionic and crystalline, and can complex monovalent metallic cations. Graft copolymers offer all properties of block copolymers but are usually easier to synthesize. Moreover, the branched structure leads to decreased melt viscosities which is an important advantage for processing.

Depending on the nature of their backbone and side chains, they give rise to special properties in selective solvents, at surfaces as well as in the bulk, owing to microphase separation morphologies [1]. They can be used for a wide variety of applications, such as polymeric surfactants, electrostatic charge reducers, compatibilizers in polymer blends, polymeric emulsifiers, controlled wetting ability and so on [2, 3]. In order to prepare graft copolymers with well-defined structure, one can utilize the macromonomer technique (grafting through technique). Well-defined structure graft copolymers are synthesized by copolymerization of macromonomers with low molecular weight comonomers [4]. It allows the control of the polymer

structure which is given by three parameters: (i) chain length of side chains, which can be controlled by the synthesis of the macromonomer by living polymerization; (ii) chain length of backbone, which can be controlled in a living copolymerization; (iii) average spacing of the side chains, which is determined by the molar ratio of the comonomers and the reactivity ratio of the low-molecular weight monomer. However, the distribution of spacing may not be very easy to control due to the incompatibility of the polymer backbone and the macromonomers [5]. As pointed out in recent publication reviews [6], there is a complex interplay of factors that govern the reactivities in copolymerizations involving macromonomers. When different comonomers are copolymerized with the same macromonomer, it seems that the degree of interpenetration between the macromonomer and the propagating copolymer backbone plays a major role in the measured reactivities. Nevertheless, the main properties depend on both the average composition of the systems and the microstructural distribution of the comonomer sequences along the macromolecular backbone, which is determined by the reactivity ratios of the macromonomer and the corresponding comonomer in the free radical polymerization process [7, 8, 9].

This work deals with the preparation and characterization of new organo-soluble associative copolymers based on short hydro-soluble chains of poly(1,3 dioxolane) (PDXL). Many reports have been published on PDXL macromonomers used to form hydrogels [10-16], however, very few were on graft copolymers with PDXL branches [17]. The present paper shows several results of the synthesis of a series of methacryloyl-terminated PDXL macromonomers by cationic ring-opening polymerization. Following their characterization, these macromonomers are used for the preparation of amphiphilic graft copolymers by solution free radical copolymerization with a hydrophobic comonomer, styrene (St) and methyl methacrylate (MMA) with the aim to obtain information about the reactivity and the polymerizability of the PDXL macromonomer. Finally, their thermal properties are discussed according to the weight content of PDXL in the copolymers.

Results and discussion

In order to obtain amphiphilic graft copolymers with controlled side chain length, PDXL macromonomers were prepared with M_n in the range of 1000-2000, bearing a methacrylic function at one of their ends, and their free radical copolymerization with vinyl and methacrylic monomers was carried out to obtain graft copolymers with hydrophobic backbone and hydrophilic side chains.

Synthesis of macromonomers

1,3 dioxolane (DXL) belongs to the class of heterocyclic monomers containing acetal functions that only polymerize cationically [18]. A specific characteristic of DXL is its lower nucleophilicity as compared to that of the acetal functions in PDXL. Thus, in competition with the propagation reaction, the active sites at the growing polymer end, i.e., cyclic dioxolenium cations will also be involved in a reaction with the acetal functions in the polymer chains [19, 20]. This continuous transacetalization process results in a broadening of the molecular weight distribution and in the formation of cyclic structures [21]. It has been shown that these intermolecular transfer reactions can be applied to introduce reactive end groups on both chain ends of PDXL by the addition of a low molar mass formal as chain transfer agent during the polymerization. The synthesis of α,ω -dihydroxy-PDXL chains is based on the activated monomer mechanism [22]. Franta et al. have established that when DXL is

polymerized by strong protonic acids, such as triflic acid, in the presence of a diol, the PDXL chains are essentially linear and carry end-standing OH functions. It has been shown that the amount of cyclic species formed is negligible, that the dispersity is on the order of 1.4 and that the molecular weight of the linear polymers is governed by the ratio of reacted monomer to transfer agent and is generally well controlled up to 10 000 g/mol.

The preparation of the methacryloyl-terminated PDXL macromonomers via 'Activated Monomer' mechanism, proposed by Franta and Reibel [22, 23], using an unsaturated alcohol (2-HPMA) as a transfer agent, results in linear polymeric chains thereby preventing formation of cyclic oligomers through cationic polymerization of cyclic acetals [24-26]. They were all prepared at the same reaction conditions. The synthetic route of functionalized PDXL macromonomers is shown in Scheme1.

Scheme1. Structures of PDXL macromonomer species [27].

According to this mechanism, it is possible to prepare macromonomers, i.e. PDXL chains carrying polymerizable double bonds at their ends. Nevertheless, because of the transacetalization reactions, a mixture of products is obtained:

A is the most abundant compound; it corresponds to 50 to 60% weight wise [27]. It is a macromonomer.

B corresponds to 20 to 25% weight wise. It is a bis-macromonomer. It carries two methacryloyl functions corresponding to transacetalization of R-OH and DXL.

C corresponds to 20 to 25% weight wise. It carries no methacryloyl function, but two hydroxyl groups. It is a α,ω -dihydroxy-PDXL.

These 3 species A, B and C stem from scrambling reactions that are typical with cyclic acetals [27].

Characterization of macromonomers

The characterization of these materials is based on structure and molecular weight determination. For instance, the PDXL macromonomers carried at one of their ends a double bond afforded by the methacryloyl group. The latter was checked by Raman and ^1H -NMR. spectroscopy. All macromonomers prepared displayed functionality close to unity, which makes them suitable for the synthesis of graft copolymers.

Raman spectroscopy is used to study and analyse the structure of the macromonomers. The aim of this study is to check the formation of linear polymer chains as well as the termination with methacryloyl groups. The spectra obtained exhibit two intense Raman bands at 800 to 900 cm^{-1} , and, 2700 to 3000 cm^{-1} regions, and a series of small other peaks for all samples as shown in Fig.1. The most intense band (2700 – 3000 cm^{-1}) is assigned to the aliphatic stretching vibration of CH in the polyacetal chain. Symmetric COCO stretching frequencies of aliphatic acetals fall in typical regions of 1115-1080 cm^{-1} and 870-800 cm^{-1} [28] and are responsible for intense Raman bands. In the low frequency region, there are three very characteristic Raman bands in the 600-550 cm^{-1} , 540-450 cm^{-1} and 400-320 cm^{-1} ranges which are assigned to COCO deformations [28, 29]. Also, the acetals have strong multiple bands in the region of 1160-1040 cm^{-1} as noticed on the Raman spectra, involving the C-O stretching modes. In addition to this, the O-CH-O group gives rise to a band at 1350-1325 cm^{-1} for C-H deformation. Other intense Raman bands are observed in the region of 3000-2700 cm^{-1} . Below 3000 cm^{-1} , the corresponding frequencies are assigned to the aliphatic C-H stretching modes [28]. The methoxy group is detected in the region of 2835-2780 cm^{-1} .

Fig. 1. Raman spectra of methacrylic-terminated PDXL macromonomers (FPP₂, FPP_{1.5} and FPP₁).

As far as the presence of the methacryloyl group in the polymeric chain is important, bands have been observed at 1640 cm^{-1} which corresponds to C=C bonds. The carbonyl compounds absorb strongly within 1900-1550 cm^{-1} region [28, 29], the spectra show a C=O bond absorption found at 1720 cm^{-1} . In the region of 1340 -1250 cm^{-1} , the methacrylate bands are observed. Broad absorption is found near 3500 cm^{-1} owing to stretching of the OH bonds. OH deformation bands are found at 1400 cm^{-1} and 1340 cm^{-1} . This observation indicates that both methacrylic and –OH groups are present and eventually the resulting product is a mixture of the three species as shown in the scheme above.

Typical ^1H -NMR spectrum of PDXL macromonomer shown in Fig. 2, exhibits the expected resonance assigned to the methoxy protons (4.77 ppm) and $\text{OCH}_2\text{CH}_2\text{O}$ protons at 3.74 ppm. Two signals corresponding to $=\text{CH}_2$ were observed at (6.12 - 6.14 ppm) and (5.57 - 5.59 ppm). Therefore the spectrum confirmed the existence of methacryloyl- terminated PDXL macromonomer.

Fig. 2. ^1H -NMR spectrum of PDXL macromonomer CDCl_3 (sample FPP₁).

Besides the structure, ^1H -NMR enables us to determine the number-average molecular weight (M_n). In the calculation of the latter, the methacryloyl end group was included. The polydispersity index, M_w/M_n , and the number-average molecular weight were obtained from SEC measurements. Table 1 summarizes these values. It can be seen that M_n (SEC) and M_n (NMR) are very close to each other for all macromonomer samples and are in agreement with the theoretical values predicted from calculations. Under our polymerization conditions, the polydispersity index is 1.6 for all samples.

Tab. 1. Characteristics of PDXL macromonomers prepared at different degrees of polymerization.

Sample	D_p	M_{nth}	M_{nSEC}	M_{nRMN}	M_w/M_n SEC	$f^{(a)}$
FPP ₁	13.5	1000	1120	1160	1.6	0.97
FPP _{1.5}	20.25	1500	1540	1550	1.6	0.99
FPP ₂	27.0	2000	2040	2100	1.6	0.97

D_p : degree of polymerization = $[\text{DXL}]/[\text{2HPMA}]$

a: functionality of macromonomers (methacryloyl end groups /molecule).

Synthesis and structural characterization of copolymers

Copolymerization of PDXL macromonomers with MMA and ST in THF solution was studied for different molar feed ratio of PDXL. The amounts of monomeric units in the copolymers were determined by elemental analysis. The results are presented in Table 2 and 3 which summarise the characteristics of the graft copolymers in terms of macromonomer feed ratio (M_2/M_1) and average M_n obtained from SEC as well as copolymer composition in weight and mole percentages which is determined from $^1\text{H-NMR}$.

Tab. 2. Characteristics of PDXL macromonomers (M_1) copolymerized with Styrene (M_2).

Sample	M_1	M_2/M_1	M_1 in the feed		M_1 in the copolymer		M_n SEC	M_w/M_n SEC
			wt(%)	mol(%)	wt(%)	mol(%)		
2SP ₂	FPP ₂	20	49	4.76	40.25	3.37	9200	1.62
3SP ₂	FPP ₂	30	39	3.22	30.3	2.21	8900	1.62
5SP ₂	FPP ₂	50	27.7	1.96	21	1.3	7200	1.59
2SP _{1.5}	FPP _{1.5}	20	41.8	4.76	34	3.4	9100	1.57
3SP _{1.5}	FPP _{1.5}	30	32.3	3.22	24	2.14	7000	1.61
5SP _{1.5}	FPP _{1.5}	50	22.4	1.96	15.2	1.2	6700	1.47
2SP ₁	FPP ₁	20	32.3	4.76	30	4.27	9200	1.78
5SP ₁	FPP ₁	50	16	1.96	14.24	1.7	5800	1.58
8SP ₁	FPP ₁	80	10.7	1.23	8.5	0.95	11900	1.95

Tab. 3. Characteristics of PDXL macromonomers (M_1) copolymerized with MMA (M_2).

Sample	M_1	M_2/M_1	M_1 in the feed		M_1 in the copolymer		M_n SEC	M_w/M_n SEC
			wt(%)	mol(%)	wt(%)	mol(%)		
2MP ₂	FPP ₂	20	50	4.76	35	2.6	21900	1.98
3MP ₂	FPP ₂	30	40	3.22	21	1.3	25900	1.57
5MP ₂	FPP ₂	50	28.6	1.96	13	0.7	87200	4.55
2MP _{1.5}	FPP _{1.5}	20	41.6	4.5	28	2.5	19800	1.93
3MP _{1.5}	FPP _{1.5}	30	33.3	3.22	22	1.8	15200	2.77
5MP _{1.5}	FPP _{1.5}	50	23	1.96	13	1.0	24700	1.6
2MP ₁	FPP ₁	20	33.3	4.76	26	3.4	21100	3.19
3MP ₁	FPP ₁	30	33.3	3.22	19	2.2	17100	1.97
5MP ₁	FPP ₁	50	20	1.96	10	1.1	13900	3.54

The structure of the copolymers was well defined by ^1H -NMR analysis. The copolymer ^1H -NMR spectra confirm the formation of copolymers, see figures: Fig. 3, and Fig. 4. The chemical shifts of protons of polystyrene and PDXL can be clearly distinguished.

Fig. 3. ^1H -NMR spectrum of styrene – PDXL copolymer in CDCl_3 (sample 3SP₂).

Fig. 4. ^1H -NMR spectrum of MMA – PDXL copolymer in CDCl_3 (sample 2MP₂).

The following peaks are assigned for: OCH₂O protons at 4.78 ppm and OCH₂CH₂O protons at 3.75 ppm, (5H, C₆ H₅) at 7.28, 7.11 and 7.06 ppm as shown in Fig. 3. The spectrum of PMMA-PDXL copolymer is shown in Fig. 4 where the chemical shifts of PMMA correspond to the proton resonance as depicted in the figure: the O-CH₃ protons are observed at 3.61 ppm and clear resonance assigned to the methyl group protons at 0.85-1.03 ppm, and eventually, we observe the corresponding chemical shifts for OCH₂CH₂O protons (3.74 ppm) and OCH₂O protons (4.77 ppm) to confirm the incorporation of PDXL in the copolymer.

Monomer reactivity ratios

The application of the classical treatment based on linearization of the copolymerization equation of Mayo and Lewis [30] or the non-linear least-squares approach suggested by Tidwell and Mortimer [31], requires working with high macromonomer concentrations (i.e. feed compositions higher than 20-30% of macromonomer) [9].

The Mayo–Lewis equation (1), that relates the instantaneous compositions of the monomer mixture to the copolymer composition, is approximated to a simplified form (equation (2)) suggested by Jaacks [32] when working with a large excess of one of the comonomers. This is the case of copolymerization reactions between a conventional comonomer and a macromonomer of relatively high molecular weight, where using low molar concentrations of macromonomer is mandatory due to its restricted solubility and the extremely viscous media.

$$\frac{d[M_1]_t}{d[M_2]_t} = \frac{[M_1]_t r_1 [M_1]_t + [M_2]_t}{[M_2]_t [M_1]_t + r_2 [M_2]_t} \quad (1)$$

$$\frac{d[M_2]_t}{d[M_1]_t} = r_2 \frac{M_2}{M_1} \quad (2)$$

Tab. 4. Monomer reactivity ratios for copolymerization of PDXL macromonomers (M₁) with St and MMA (M₂).

Sample	M ₂	M ₁ macromonomer	M _{nth}	r ₂	1/r ₂
SP ₂	St	FPP ₂	2000	0.12 ± 0.006	8.33
SP _{1.5}	St	FPP _{1.5}	1500	0.042 ± 6 · 10 ⁻⁴	23.8
SP ₁	St	FPP ₁	1000	0.015 ± 3 · 10 ⁻⁴	66.66
MP ₂	MMA	FPP ₂	2000	0.02 ± 0.01	50
MP _{1.5}	MMA	FPP _{1.5}	1500	0.07 ± 0.02	14.28
MP ₁	MMA	FPP ₁	1000	0.018 ± 0.01	55.55

According to equation (2), the copolymer composition or the frequency of branches is essentially determined by the monomer composition and the monomer reactivity ratio of the comonomer r₂ (inversely proportional to the macromonomer reactivity), under the limit condition of [M₂]/[M₁] >>1. In order to obtain reliable values, it is frequently necessary to run the copolymerization at different conversions or to carry out several

copolymerizations with different initial monomer ratios [33]. In such cases, an integrated form of equation (2) is used:

$$\ln \frac{[M_2]_t}{[M_2]_0} = r_2 \ln \frac{[M_1]_t}{[M_1]_0} \quad (3)$$

where $[M_i]_t/[M_i]_0$ is the ratio among the composition of monomer i at time t and the initial feed composition. A plot of $\ln([M_2]_t/[M_2]_0)$ versus $\ln([M_1]_t/[M_1]_0)$ should result in a straight line with a slope that equals to r_2 (the reactivity ratio of the comonomer).

Fig. 5. Application of Jaacks' treatment to the St-PDXL copolymerization systems: (a) SP_1 (b) $SP_{1.5}$ (c) SP_2 .

Thus, the monomer reactivity ratios between the PDXL macromonomers and the comonomers were estimated with the data in Tables 2 and 3. We can apply equation (3) to the estimation, where M_1 and M_2 are the PDXL macromonomer and copolymer respectively. The monomer reactivity ratios are determined for macromonomers of different M_n (degree of polymerization) and summarized in Table 4.

Fig. 6. Application of Jaacks' treatment to the MMA-PDXL copolymerization systems: (a) MP_1 (b) $MP_{1.5}$ (c) MP_2 .

In the case of copolymerization with Styrene and MMA, the results suggest that the reactivity of the methacrylic double bond in the prepared macromonomers is not affected in their copolymerization with Styrene or MMA. This point is confirmed when analysing the inverse ratio $1/r_2 = k_{21}/k_{22}$, which is sometimes considered as the relative copolymerization reactivity of a macromonomer [34]. This quantity is the ratio between the crosspropagation and homopropagation rate constants of comonomer 2,

which is directly proportional to the reactivity of the macromonomer (1) and gives a clear idea of the relative reactivity of a growing radical ending in 2 units towards the addition of monomer 1, in comparison to the tendency for the homopropagation. So, we have a situation where $r_1 \gg 1 \gg r_2$, and it is expected that the initially formed chains should contain more macromonomers, and then more comonomer segments are added. These are only assumptions, but they give an indication about the probable composition drift of the graft copolymers obtained. On the other hand, in the case of copolymerization of poly(1,3 dioxolane) macromonomers with styrene (Fig. 5), the results show that r_2 increases with increasing PDXL side chain length (in terms of average M_n) and this leads to say that the side macromonomer chain length affect the reactivity of the comonomer. Thus, this indicates that a growing radical of macromonomer with a shorter chain length (i.e. lower M_n) attacks more frequently a monomer of the same nature than it does a macromonomer with a longer length (i.e. higher M_n), as it can be noticed from the results in Table 4. However, the r_2 values of the copolymerization with MMA (Fig. 6) give unclear dependence on the side poly(1,3 dioxolane) macromonomer chain length; this may be due to the resulting polydispersity of the copolymerization. Mentioned behaviour may be related to the reactive structure of comonomers, vinyl in the case of styrene or methacrylic in the case of MMA, in regard to the ending methacrylic double bond of macromonomers, besides the hydrophilic character of the macromonomers.

Glass transition temperatures

In the first place, the measurements of transition temperatures were performed on a conventional DSC from which the thermograms obtained show an overlapping of PS glass transition temperature and PDXL melting point signals. This has been observed for all samples.

Fig. 7. MTDSC thermogram of 5SP₁ copolymer at heating rate of 2 °C/min.

A different approach in the characterization of these copolymers was by using a Modulated Temperature Differential Scanning Calorimeter Q100 TA instrument (MTDSC) which is an extension of conventional DSC that combines high resolution with high sensitivity by use of a sinusoidal temperature modulation superimposed on a constant temperature or linear temperature program with a small underlying average heating rate [35, 36]. In comparison to conventional DSC, the MTDSC analysis enables the simultaneous calculations of an additional quantity, the cyclic or modulus of heat capacity, C_p ($\text{J g}^{-1}\text{K}^{-1}$) [35]:

$$C_p = \frac{A_{HF}}{A_T \omega} \quad (4)$$

where A_{HF} is the amplitude of the cyclic heat flow (Wg^{-1}) and $A_T \omega$ is the amplitude of cyclic heating rate, with A_T the temperature modulation amplitude (K), ω the modulation angular frequency ($2\pi/p$) and p is the modulation period (s) [35]. In fact, the MTDSC splits the overlapped signals into two distinct temperatures, melting temperature of the hydrophilic grafts and glass transition temperature of the hydrophobic backbone as can be noticed in Fig. 7 in which melting temperature appears to be 56.26°C which is closer to the glass transition temperature with a value of 56.71°C .

Tab. 5. Transition temperatures of styrene-PDXL copolymers obtained by thermal analysis (DSC).

Sample	PDXL content wt(%)	T _g (°C)
8SP ₁	8.5	74.89
5SP ₁	14.24	56.71
5SP _{1.5}	15.2	55.90
5SP ₂	21	67.39
3SP ₂	30.3	44.80
2SP _{1.5}	34	26.65
2SP ₂	40.25	40.60

Tab. 6. Transition temperatures of MMA-PDXL copolymers obtained by thermal analysis (DSC).

Sample	PDXL content wt(%)	T _g (°C)
5MP ₁	10	105.45
5MP _{1.5}	13	82.78
3MP ₂	21	65.76
3MP _{1.5}	22	75.50
2MP ₁	26	70.13

From these measurements, T_g was taken at the midpoint of the transition region. The results obtained are shown in Tables 5 and 6 for copolymers with styrene and MMA respectively. Then, a plot of the copolymers T_g has been constructed against PDXL content in order to study the effect of the latter on T_g 's. As it can be noticed in the Fig. 8, T_g of the copolymers decreases exponentially with increasing PDXL content and this may be due to the decrease in the intermolecular interactions between the

molecular chains and can be associated with higher mobility and flexibility of the polymeric chains when PDXL is incorporated in the copolymers. The results clearly indicate that T_g values of the copolymers depend on the composition of comonomers and decrease with increasing PDXL content in the obtained copolymers.

Fig. 8. Glass transition temperatures vs. PDXL macromonomer content for copolymer systems: (a) styrene-PDXL copolymers; (b) MMA-PDXL copolymers.

Conclusions

Methacrylate-terminated PDXL macromonomers were copolymerized with St and MMA using different feed molar ratios. Both feed molar ratio and the size of the graft influence the composition of the copolymers. The macromonomer reactivity estimation suggests that the length of the PDXL side chains does affect the reactivity of the methacrylic double bond of the macromonomer when copolymerized with St. However, in the case of copolymerization with MMA, there is no dependence on the graft size. Finally, from DSC measurements, the values of T_g depend on the composition and the size of the PDXL grafts. In all copolymers, the increase in amount of the incorporated PDXL macromonomer results in a substantial decrease in glass transition.

Experimental part

Materials

The monomer 1,3 dioxolane (DXL) and 2-hydroxypropyl methacrylate (2-HPMA) of commercial grades were purchased from Acros. DXL was kept under KOH for two to three days to remove any peroxide and stabiliser traces and then purified by distillation over CaH_2 prior to polymerization. Trifluoromethanesulfonic acid (triflic acid, Aldrich) was used as received. Commercially available styrene (St) and MMA (Prolabo) were purified by distillation over CaH_2 at reduced pressure. CH_2Cl_2 and THF commercially available from Prolabo were purified by conventional methods [15, 37]. 2,2-Azobisisobutyronitrile (AIBN) recrystallized from methanol was used. All chemicals were kept over molecular sieve before use.

Macromonomer Synthesis

Methacrylate-terminated PDXL macromonomers were synthesized by Cationic ring-opening polymerization which was carried out in 10 ml dichloromethane with triflic acid as initiator at room temperature under nitrogen for 24 h, in the presence of 2-hydroxypropyl methacrylate (2-HPMA) as transfer agent. 20 ml of DXL monomer was added. The feed molar ratios $[\text{DXL}]/[\text{2-HPMA}]$ as well as the molecular characteristics of the obtained macromonomers are reported in Table 1. The amount of the acid used was 20 μl . After reaction, the resulting solution was poured into THF. Then, the product was purified by re-precipitation from THF solution with a large excess of hexane and the obtained polymer was dried under vacuum at room temperature. The yield was checked by gravimetric determination and found to be about 80%.

Copolymer Synthesis

PDXL macromonomers of different molecular weights were copolymerized with St and MMA in THF at 60 °C in the presence of 2,2'-azobisisobutyronitrile, AIBN, (1%, based on the total weight of the monomers) as initiator, under a nitrogen atmosphere, using different feed molar fractions of macromonomers.

Tab. 7. Copolymerization of PDXL macromonomers (M_1) with styrene (M_2).

Sample	M_1	M_2/M_1	PDXL			Styrene		AIBN (g)	THF (ml)	Conc. (mol/l)
			(g)	(mol)	(g)	(mol)	(ml)			
2SP ₂	FPP ₂	20	3.49	$17.45 \cdot 10^{-4}$	3.64	$3.49 \cdot 10^{-2}$	4	0.07	60	0.610
3SP ₂	FPP ₂	30	2.32	$11.6 \cdot 10^{-4}$	3.64	$3.49 \cdot 10^{-2}$	4	0.06	60	0.601
5SP ₂	FPP ₂	50	1.4	$6.98 \cdot 10^{-4}$	3.64	$3.49 \cdot 10^{-2}$	4	0.05	60	0.593
2SP _{1.5}	FPP _{1.5}	20	2.62	$17.45 \cdot 10^{-4}$	3.64	$3.49 \cdot 10^{-2}$	4	0.06	60	0.610
3SP _{1.5}	FPP _{1.5}	30	1.74	$11.6 \cdot 10^{-4}$	3.64	$3.49 \cdot 10^{-2}$	4	0.06	60	0.601
5SP _{1.5}	FPP _{1.5}	50	1.05	$6.98 \cdot 10^{-4}$	3.64	$3.49 \cdot 10^{-2}$	4	0.05	60	0.593
2SP ₁	FPP ₁	20	1.74	$17.45 \cdot 10^{-4}$	3.64	$3.49 \cdot 10^{-2}$	4	0.06	60	0.610
5SP ₁	FPP ₁	50	0.7	$6.98 \cdot 10^{-4}$	3.64	$3.49 \cdot 10^{-2}$	4	0.05	60	0.593
8SP ₁	FPP ₁	80	0.436	$4.36 \cdot 10^{-4}$	3.64	$3.49 \cdot 10^{-2}$	4	0.05	60	0.589

The total monomer concentration was $6 \times 10^{-1} \text{M}$ in all cases. The copolymerization product was diluted with THF and then added dropwise to a large excess of methanol to remove unreacted PDXL macromonomers [38, 39]. The polymers were finally dried over vacuum at 40°C to constant weight. The yields of all reactions were 70–90%. Tables 7 and 8 summarize the amount of all reagents used for the copolymerizations.

Tab. 8. Copolymerization of PDXL macromonomers (M_1) with MMA (M_2).

Sample	M_1	M_2/M_1	PDXL (g)	PDXL (mol)	MMA (g)	MMA (mol)	ml	AIBN (g)	THF (ml)	Conc. (mol/l)
2MP ₂	FPP ₂	20	3.74	18.7×10^{-4}	3.744	3.74×10^{-2}	4	0.08	65	0.604
3MP ₂	FPP ₂	30	2	10×10^{-4}	3.00	3.00×10^{-2}	3.2	0.05	50	0.620
5MP ₂	FPP ₂	50	1.5	7.48×10^{-4}	3.744	3.74×10^{-2}	4	0.05	60	0.636
2MP _{1.5}	FPP _{1.5}	20	2	13.3×10^{-4}	2.8	2.80×10^{-2}	3	0.05	25	1.00
3MP _{1.5}	FPP _{1.5}	30	1.87	12.5×10^{-4}	3.744	3.74×10^{-2}	4	0.06	60	0.644
5MP _{1.5}	FPP _{1.5}	50	1.12	7.48×10^{-4}	3.744	3.74×10^{-2}	4	0.05	60	0.636
2MP ₁	FPP ₁	20	2	20×10^{-4}	4.00	4×10^{-2}	4.3	0.06	50	0.840
3MP ₁	FPP ₁	30	1.25	12.5×10^{-4}	3.744	3.74×10^{-2}	4	0.05	64	0.604
5MP ₁	FPP ₁	50	0.75	7.48×10^{-4}	3.744	3.74×10^{-2}	4	0.05	60	0.636

Characterization

Raman spectroscopy was used to study and analyse the structure of the macromonomers. Number-average molecular weights (M_n) and polydispersity indices (M_w/M_n) were determined by Size Exclusion Chromatography (SEC) and $^1\text{H-NMR}$. SEC Measurements were performed at 40°C on a Waters 2690 instrument equipped with UV detector (Waters 996 PDA) coupled with a Differential Refractometer (ERC - 7515 A) and four Styragel columns (10^6 , 10^5 , 500 and 50°A). THF was employed as a solvent with 1 ml/min flow rate. Polystyrene standard samples were used for calibration. $^1\text{H-NMR}$ spectra were recorded on Advance Bruker spectrometer. Deuterated chloroform was used as solvent. DSC measurements were performed on a Modulated Temperature Differential Scanning Calorimeter Q100 TA instrument, under nitrogen at 50 ml/min. The samples were hermetically sealed in aluminium pans and they were subjected to a heating program as follows:

- ramp of $5^\circ\text{C}/\text{min}$ to 80°C
- a ramp of $2^\circ\text{C}/\text{min}$ to -60°C
- then an isothermal for 5 min
- finally a ramp of $2^\circ\text{C}/\text{min}$ to 80°C .

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