Synthesis of Syndiotactic Star Poly(methyl methacrylate)s with Controlled Number of Arms

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Introduction. Since the first attempt to synthesize polymers with star configuration by Schaefgen and Flory,[1] and particularly after the route opened by the discovery of anionic polymerization,[2] the synthesis of this type of topologically controlled structures has attracted a growing attention in research. The interest that star polymers awakened owing to their peculiar solution properties and rheological behavior[3] has led to the development of several complementary techniques of synthesis, mainly living polymerization methods,[4] which offer different degrees of control of both the core structures and the compositional homogeneity.[5] It is noteworthy that, among them, primarily living polymerization in the presence of a multifunctional initiator or coupling reaction of linear living polymers with a multifunctional coupling agent can afford a predetermined number of arms per molecule.

Typically, the use of chlorosilanes as linking agents is the method of choice for the preparation of stars with well-controlled core structure. Such a powerful approach has permitted the preparation of homostars,[3a,6] block star copolymers,[7] and miktoarm stars,[8] where the arms may be polystyrene, polyisoprene, polybutadiene, or poly(4-methylstyrene). On the other hand, the direct incorporation of living poly(methacryllithium) seemed impossible,[9] as further investigated during this research.[10] The preparation of star poly(methyl methacrylate)s (PMMAs) has been possible by other methods, such as group transfer polymerization,[11] even though stars with predetermined arm numbers were synthesized only in few cases, by either core-first approaches[12] or isolating the intermediate products (i.e., functionalized arms) prior to the coupling reaction.[13] Also, in miktoarm stars the incorporation of PMMA branches was performed by using the macromonomer approach[14] or through a macromonomer initiator.[9]

In this paper we report a general arm-first approach for the synthesis of star PMMAs with well-defined structures which does not require any isolation of intermediates or preparation of macromonomers. Excess of living poly(methacryllithium) arms with syndiotactic structure was directly coupled with multifunctional bromomethylbenzenes to obtain 4- and 6-branch polymers. The straightforward control of the structural homogeneity exemplified through the one-step preparation of such PMMAs also permitted their direct characterization by ^{1}H NMR, in terms of chain ends, tacticity, core structure, and molecular weights.

Experimental Section. MMA was purified by distillation under reduced nitrogen pressure and distilled again over CaH_2 under high vacuum, just before use. t-C_4H_9Li and 1,1-diphenylethylene (DPE) were obtained commercially. Tetrahydrofuran (THF) was refluxed over CaH_2 and then over $LiAlH_4$, stored with $LiAlH_4$, and distilled under vacuum before use. The coupling agents, 1,4-bis(bromomethyl)benzene (BBMB), 1,2,4,5-tetrakis(bromomethyl)benzene (TBMB), and hexakis(bromomethyl)benzene (HBMB), were used as received after being accurately dried.

The polymerization of MMA was carried out at −78 °C in 5 mL of THF in a glass ampule filled with dried nitrogen, by using an initiator prepared in situ at 0 °C by reacting DPE with t-C_4H_9Li, used as heptane solution, and following the procedure already reported elsewhere[15] for the preparation of syndiotactic chains. After 3 h of polymerization, the multifunctional bromomethylbenzene was slowly added as THF solution to the excess of living macromolecules and allowed to react for 16 h at −78 °C. This procedure was followed in order to ensure complete reaction with all the active centers of the coupling agents.[16] The uncoupled chains were terminated by adding methanol containing aqueous HCl (1 N). It is also worth stating that the low solubility of HBMB in THF involved the addition of a remarkable amount of coupling solution, and in order to facilitate the maintenance of the reaction temperature, it was necessary to use an ampule with a double tube. Thus, at the due time the addition simply occurs by accurately mixing polymer and HBMB solutions contained in the two parts, both already at −78 °C.

Size exclusion chromatography measurements were performed on a Jasco 880-PU chromatograph equipped with two GPC columns Shodex KF-806L at 40 °C using THF as eluent or on a Jasco 980-PU equipped with two analytical PL gel columns (300 × 7.5 mm i.d.) packed with poly(styrene-*co*-divinylbenzene) beads (pore size marked as Mixed E, particle size 3 μm), operating at 35 °C, and a differential refractometer as detector (SEC-RI). ^{1}H NMR spectra were measured in nitrobenzene-d_5 at 110 °C on a JEOL JNM-GSX270 at 270 MHz or a Varian Unity-Inova 500 spectrometer at 500 MHz.

Results and Discussion. The reaction of living PMMA solution with electrophiles such as vinylbenzyl iodide or bromide and allyl bromide was already reported to occur with high efficiency,[17] and the same approach was also used for the synthesis of PMMA macromonomers.[18] Following this route, the reaction of stereoregular living chains prepared either in polar or nonpolar solvents was attempted using different multifunctional agents.[19] No coupling was observed in nonpolar solvents, while in THF the reaction with bromethylbenzenes proceeds quantitatively.

A series of syntheses were performed with living syndiotactic PMMAs having low molecular weights capped by TBMB and HBMB, as summarized in Table 1, where the results of equimolar coupling reactions

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Table 1. Synthesis and Molecular Characteristics of PMMAs with Predetermined Number of Arms

	polymerization conditions		precursor			coupling byproduct			
run	[MMA]/[In][a]	[In]/[CA][b]	$M_n \times 10^{-3\,c}$	$M_w/M_n{}^c$	$M_n \times 10^{-3\,d}$	$M_n \times 10^{-3\,c}$	$M_w/M_n{}^c$	n^e	$M_n \times 10^{-3\,f}$
2S1	15	2				3.4	1.04	2.0	3.7
2S2	40	2				8.9	1.06	2.0	9.1
4S1	25	10	2.9	1.06	3.0	9.2	1.04	4.0	12.1
4S2	60	7	6.2	1.09	6.1	16.2	1.06	3.9	24.1
6S1	25	10	3.3	1.06	3.1	9.6	1.06		18.9
6S2	75	10	6.8	1.08	7.7	18.6	1.05		46.1

[a] Ratio monomer to initiator, where 5−10 mM of monomer was used, depending on the final viscosity of the mixture. Monomer conversion 100%. [b] Ratio initiator to coupling agent, where the agents are BBMB, TBMB, and HBMB for **2S**s, **4S**s, and **6S**s, respectively. In the case of TBMB and HBMB the lowering of temperature down to −78 °C induced their partial precipitation from the almost saturated solution; hence, the ratios reported for **4S**s and **6S**s must be considered only as indicative of the initial concentration. [c] Determined by SEC-RI calibrated to PMMA standards. [d] Calculated by ^{1}H NMR from the intensities of the methoxy proton signal and the signals of the methyl protons of the initiator residue. [e] Arm number per macromolecule calculated by ^{1}H NMR as end groups from the integration ratio of the methyl protons of the initiator residue to the aromatic protons of the coupling agent residue. [f] Calculated by ^{1}H NMR as for the precursor, considering the number of arms, either calculated or deduced.

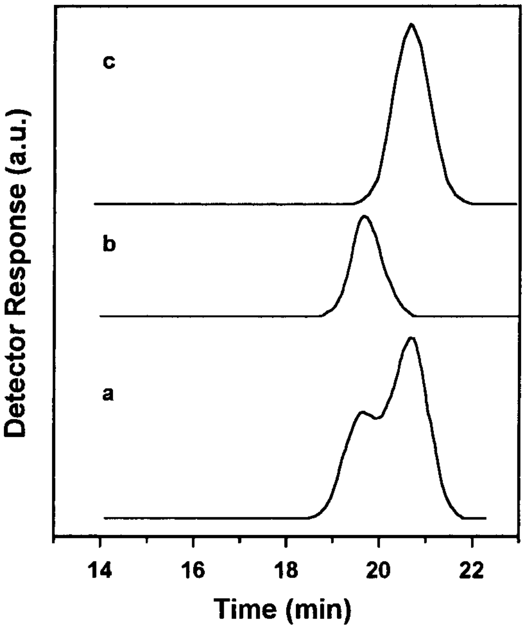

Figure 1. SEC-RI charts of separation of crude sample **4S2** (a) and two fractions (b and c) obtained thereof by the liquid adsorption chromatography/full adsorption method.

with BBMB are also reported as reference. The reaction mixtures showed bimodal size exclusion chromatograms such as the one reported in Figure 1a, relative to the run **4S2**. In any sample, the molecular weight (*M*) of the peak at longer retention times, i.e., the precursor, well agrees with the calculated value of the starting living polymer as well as with that determined by NMR. On the other hand, the monodisperse shorter retention time peak, potentially corresponding to star PMMA, presents values of *M* always lower than those calculated from NMR. This apparent inconsistency is intrinsic in the basis of the SEC separation process. Since in star polymers the molecular hydrodynamic volume does not grow linearly with the number of arms, the values determined by SEC-RI inevitably appear underestimated in comparison with the calculated ones.[20] In reason of the relative similarity between the hydrodynamic volumes of single arm and star polymer, it is hardly possible to resolve each single constituent of polymer mixture, and other chromatographic techniques have been suggested. The theoretical and experimental details of their successful fractionation will be discussed in a forthcoming paper,[21] and the molecular characteristics of the separated fractions are listed in Table 1. In Figure 1b,c are reported as example the curves of the linear and the 4-arm PMMAs, respectively, fractionated by liquid adsorption chromatography/full adsorption method.

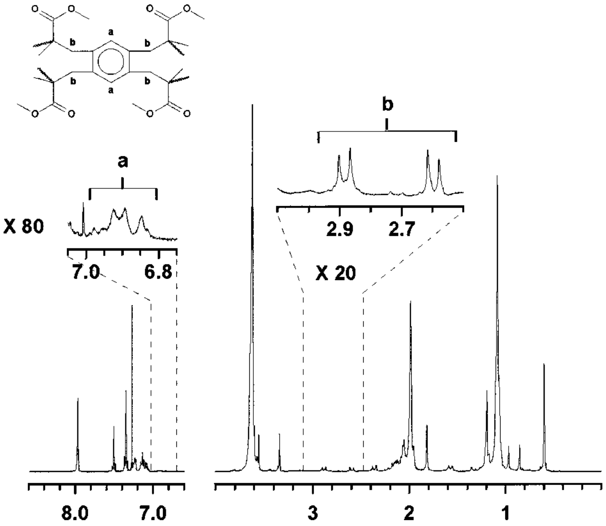

Figure 2. The 500 MHz ^{1}H NMR spectrum of 4-arm PMMA in nitrobenzene-d_5 at 110 °C (coupling product with TBMB, run **4S1**).

^{1}H NMR spectra of any fraction eluted at longer retention times showed the typical pattern of syndiotactic PMMAs (mm:mr:rr = 2:17:81),[15] presenting a peak at 2.5 ppm due to the terminal methine protons of the racemo diad.[22] The peak intensity ratio itself to any main chain signal is in good agreement with the complete linearity of such molecules.

By comparing the spectra of the coupling byproducts with those of the corresponding bromomethylbenzenes and of the linear PMMA, it was possible to point out the core structure and verify the reaction efficiency as well. As general finding, the calculated average number of units per branch has always the same value in both the separated coupling product and the corresponding precursor polymer. A typical ^{1}H NMR spectrum of the coupling product with TBMB, relative to run **4S1**, is shown in Figure 2. In all the capped polymers two new doublets are clearly visible at around 2.6 and 2.9 ppm, which may be assigned to methylene protons adjacent to the aromatic ring, tentatively in a structure type $C_6H_{6-n}-(CH_2-C-)_n$.[18b] At the same time, no resonances for the terminal methine protons and for the bromomethyl groups at 4.5−4.7 ppm are observed, nor signals due to secondary reaction products of such groups. The capping of the PMMA chains is also inferred by new resonances at 6.8−7.0 ppm of the aromatic protons of the BBMB and TBMB fragments, and their complete capping is directly confirmed by the integration ratio of the methyl protons of the initiator (t-C_4H_9Li) residue to the aromatic protons of the core, which yields end groups per star polymer molecule almost coincident with the theoretical number of arms (Table 1). On the other hand, in the case of 6-armed PMMAs the completion of coupling reaction is deduced mainly on the basis of the absence of residual bromomethyl groups, which, taking into account the precision of the specific NMR measurements, could be revealed down to concentration corresponding to less than 1×10^{-3} groups per star molecule.[23]

In conclusion, we highlighted a general method for the one-step preparation of star PMMAs with controlled number of arms, eventually applicable for obtaining macromolecules having different tacticities. The results herewith presented show the synthesis of syndiotactic 4- and 6-arm stars and exemplify the feasibility of this approach, whose only limitation is intrinsic in the eventual insolubility of bromomethylbenzene derivates having higher functionality. Its simplicity is also due to the needless of time-consuming intermediate preparation and/or separation as well as to the satisfactory investigation of the structure of coupling byproducts by ^{1}H NMR. Furthermore, the same structural homogeneity allows a direct spectroscopic evaluation of both arm lengths and molecular weights.

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